Elementary Steps, the Role of Chemisorbed Oxygen, and the Effects of Cluster Size in Catalytic CH₄–O₂ Reactions on Palladium

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Supporting Information

ABSTRACT: Kinetic and isotopic data and effects of cluster size are used to probe elementary steps and their kinetic relevance in CH₄–O₂ reactions on Pd clusters that retain a metallic bulk during catalysis. CO₂ and H₂O were the only products detected, except when O₂ was nearly depleted, during which trace CO amounts were formed. \(^{13}\)CH₄–\(^{12}\)CO–O₂ reactions showed that CO reacts with chemisorbed oxygen (O*) much faster than CH₄ with reactive collision probability ratios for CO and CH₄ proportional to O₂/CO ratios via a constant exceeding 500. Thus, even if CO desorbed before forming CO₂, it would oxidize via reactions with O* at any reactor residence time required for detectable CH₄ conversion, making direct partial oxidation impractical as a molecular route to H₂–CO mixtures on Pd. CH₄ turnover rates and effective first-order rate constants initially decreased and then reached constant values as O₂ pressure and O* coverage increased as a result of a transition in the surface species involved in kinetically relevant C–H bond activation steps from O* to O*–O* site pairs (\(\equiv\) vacancy site). On O*–O* site pairs, C–H bonds are cleaved via H-abstraction mediated by O* and radical-like CH₃ fragments weakly stabilized by the vicinal O* are formed at the transition state. These reactions show large activation barriers (158 kJ mol\(^{-1}\)) but involve high entropy transition states that lead to larger pre-exponential factors (1.48 \times 10^{9} kPa\(^{-1}\) s\(^{-1}\)) than for tighter transition states involved in C–H bond activation by \(\equiv\) site pairs for CH₄ reactions with H₂O or CO₂ (barriers: 82.5 kJ mol\(^{-1}\) and pre-exponential factors: 3.5 \times 10^{5} kPa\(^{-1}\) s\(^{-1}\)). CH₃ fragments at the transition state are effectively stabilized by interactions with vacancy sites on O*–O* site pairs, which lead to higher turnover rates, as vacancies become available with decreasing O₂ pressure. CH₄–O₂ turnover rates and C–H bond activation rate constants on O*–O* site pairs decreased with decreasing Pd cluster size, because coordinatively unsaturated exposed atoms on small clusters bind O* more strongly and decrease its reactivity for H-abstraction. The stronger O* binding on small Pd clusters also causes the kinetic involvement of O*–O* sites to become evident at lower O₂ pressures than on large clusters. These effects of metal–oxygen bond strength on O* reactivity also lead to the smaller turnover rates observed on Pd clusters compared with Pt clusters of similar size. These effects of cluster size and metal identity and their O* binding energy are the root cause for reactivity differences and appear to be general for reactions involving vacancies in kinetically relevant steps, as is the case for CH₄, C₂H₆, NO, and CH₃OCH₃ oxidation on O*-covered surfaces and for hydrogenation of organosulfur compounds on surfaces nearly saturated with chemisorbed sulfur.

1. INTRODUCTION

Small Pd clusters dispersed on high surface area substrates are useful as CH₄ combustion catalysts in power generation and exhaust gas treatment.\(^1\)–\(^4\) Similar catalysts also promote CH₄–O reactions at substoichiometric ratios (O₂/CH₄ < 2) to form CO and H₂ via mildly exothermic routes.\(^3\) The latter reactions produce synthesis gas or H₂ via less endothermic routes than CH₄–H₂O/CO₂ reforming (\(\Delta H_f^{298} = 206\) kJ mol\(^{-1}\) (H₂O), 247 kJ mol\(^{-1}\) (CO₂))\(^5\)\(^6\)\(^7\) and lessen heat transfer requirements and catalyst deactivation. Autothermal reformers use O₂ in flame combustion of CH₄ in CH₄–H₂O–O₂ mixtures at the reactor inlet to provide the heat required for subsequent reforming reactions.\(^8\) These autothermal routes lead to sharp temperature profiles along the catalyst bed, which would be absent if direct catalytic partial oxidation occurred at the molecular scale or within thermal conduction distances in monoliths or packed bed reactors.

The reactions that form CO₂–H₂O\(^9\)–\(^11\) and CO–H₂\(^7\)\(^12\)–\(^14\) from CH₄–O₂ reactants on Pd have been previously examined, but the required active sites, the detailed sequence of the elementary steps, and their kinetic relevance and even whether H₂ and CO can form directly as primary products remain issues of active debate and considerable controversy. These issues reflect, at least in part, the presence of ubiquitous temperature and concentration gradients within catalyst pellets and beds as a result of the fast nature of these reactions, the typical high conversions that prevail, and the highly exothermic nature of combustion reactions (\(\Delta H_f^{298} = \approx -802\) kJ mol\(^{-1}\)). The chemical transformations between Pd and PdO bulk chemical states also complicate the mechanistic interpretation of concentration and temperature.

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effects on rate data in terms of elementary steps and their kinetic relevance. These metal-oxide transformations occur in response to changes in oxygen chemical potential and temperature as $O_2$ is depleted along the reactor or within porous catalyst pellets. These changes in chemical state can occur concurrently with structural transformations that alter the shape of such clusters and the intimacy of their contact with supports, which alter, in turn, the coverage and reactivity of oxygen atoms, as shown when surfaces of Pd foil interconvert between metal and oxide states. Here we provide evidence of the chemical origins of the rate and selectivity observed in CH$_4$–O$_2$ reactions on Pd clusters by measuring the rate of chemical events in the absence of transport corruptions in a range of oxygen chemical potentials that maintains the bulk of Pd clusters (4.5–22.3 nm) in their metallic state. Our recent studies in CH$_4$–O$_2$ reactions on Pt$^{19,20}$ and CH$_4$–H$_2$O/CO$_2$$^{21–27}$ reactions on several metals (Rh$^{21}$, Pt$^{22}$, Ir$^{24,25}$, Ni$^{26}$, Ru$^{23}$, and Pd$^{27}$) have probed the elementary steps and site requirements for these reactions. CH$_4$–H$_2$O/CO$_2$ turnover rates on Pd clusters are limited by C–H bond activation steps on *–* site pairs$^{27}$ as also found on other metals$^{21–24,26}$ but rate constants are significantly larger than those on other metals and cause C–H bond dissociation to become reversible. Fast C–H bond activation on Pd also leads to kinetically detectable coverages by C* and H* intermediates, which inhibit reforming reactions.$^{27}$ In CH$_4$–O$_2$ mixtures, O*–* and O*–O* site pairs on Pt cluster surfaces activate C–H bonds with different activation enthalpies and entropies, kinetic dependencies, and cluster size effects than the *–* site pairs that activate CH$_4$ in reactions with H$_2$O/CO$_2$. These concepts are extended here to Pd clusters, for which elementary steps and their kinetic relevance for CH$_4$–O$_2$ reactions and the selectivity of chemisorbed oxygen in reactions with CH$_4$ and CO remain uncertain.

We address the catalytic consequences of using O$_2$ as the oxidant and the role of chemisorbed oxygen (O*) in CH$_4$–O$_2$ reactions on metallic Pd clusters by measuring reaction rates and selectivities in kinetic control regime without transport artifacts. The chemical equilibrium between O* species and O$_2$(g) was confirmed by $^{16}$O$_2$–$^{18}$O$_2$ isotope exchange probe reactions. In a parallel study, we address the behavior of CH$_4$–O$_2$ reactions on PdO clusters$^{28}$ and the dynamics of Pd–PdO phase transition.$^{29}$ Kinetic and isotopic studies are used to determine the role of O* in the kinetically relevant elementary steps for CH$_4$–O$_2$ reactions and to establish that CO does not form at detectable levels during these reactions on Pd clusters.$^{13}$CH$_4$–CO–O$_2$ reactions showed that even if CO* desorbed unreacted, it would react with O* at any residence time required for detectable CH$_4$ conversion, indicating that direct partial oxidation is not feasible on Pd clusters and that CO (and H$_2$) form exclusively via sequential reforming reactions. The proposed sequence of elementary steps is consistent with rate data, CH$_4$/CO$_2$, kinetic isotope effects, oxygen exchange kinetics, and with steps that mediate CH$_4$–H$_2$O/CO$_2$ reactions on group VIII metals$^{21–24,26}$ and CH$_4$–O$_2$ reactions on Pt.$^{19,20}$ Kinetically relevant C–H bond activation steps occur on O*–O* site pairs at O*-saturated surfaces and on O*–* site pairs as O* coverages decrease below saturation. Rate constants for C–H bond activation increased with increasing Pd cluster size as a result of a concomitant decrease in O* binding energy. These kinetically relevant steps and active site structures were similar to those proposed for Pt; the rate constants were, however, smaller because O* binding is stronger on Pd than Pt clusters of similar size.

### 2. EXPERIMENTAL METHODS

#### 2.1. Synthesis of Dispersed Pd Clusters on High Surface Area Oxide Supports. γ–Al$_2$O$_3$ (Sasol North America, lot no. C1643, 193 m$^2$ g$^{-1}$, 0.57 cm$^3$ g$^{-1}$ pore volume) and SiO$_2$ (Davison Chemical, grade 923, CAS no. 112926-00-8, 280 m$^2$ g$^{-1}$, 0.85 cm$^3$ g$^{-1}$ pore volume) supports were treated in flowing dry air (Praxair, zero grade, 0.083 K s$^{-1}$, 60 cm$^3$ g$^{-1}$) at 923–1073 K for 5 h before impregnation with aqueous Pd(NO$_3$)$_2$ solutions (Aldrich, 99.999% purity, 10 wt% Pd(NO$_3$)$_2$ in 10 wt% HNO$_3$) to obtain samples containing 0.2 wt% Pd. Impregnated samples were treated in stagnant ambient air at 383 K for 8 h and then in flowing dry air (Praxair, zero grade, 60 cm$^3$ g$^{-1}$) by heating to 623 at 0.033 K s$^{-1}$ (3 h hold) and then to 923 at 0.083 K s$^{-1}$ (5 h hold) and cooling to ambient temperature. A portion of the catalysts was then treated in flowing H$_2$–Ar mixture (10% H$_2$/Ar, 0.083 K s$^{-1}$, 60 cm$^3$ g$^{-1}$, Praxair certified standard) at a temperature between 923 and 1023 K for 3 h, cooled to 673 K, and then treated in He (Praxair UHP grade, 60 cm$^3$ g$^{-1}$) at 763 K before cooling to ambient temperature. O$_2$/He mixtures (0.5% O$_2$/He, Praxair certified standard, 60 cm$^3$ g$^{-1}$) were introduced to the samples at ambient temperature for at least 2 h before exposure to ambient air. The fraction of exposed Pd atoms was determined by volumetric O$_2$ chemisorption experiments carried out on a Quantachrome Autosorb-1 unit at 313 K. The number of exposed Pd atoms was determined from extrapolation of O$_2$ adsorption isotherm to zero pressure with the assumption that the atomic ratio of oxygen-to-exposed Pd equals one and Pd clusters are in hemispherical shapes with a metal density of bulk Pd (12.0 g cm$^{-3}$).$^{30}$

#### 2.2. Measurements of CH$_4$–O$_2$ Turnover Rates and O$_2$ Selectivities. Steady-state CH$_4$ conversion turnover rates were measured at 873–973 K in a tubular flow reactor (quartz; 8.1 mm inner diameter) with plug flow hydrodynamics. Catalysts were diluted with inert SiO$_2$ (Davison Chemical, Chromatographic Silica Media, CAS no. 112926-00-8, 280 m$^2$ g$^{-1}$) to a diluent-to-catalyst mass ratio of 50–200, pelletized, and sieved to retain 106–250 μm aggregates. These particles were then mixed with quartz (Fluka, acid purified, product number 48880, 106–250 μm diameters) at a diluent-to-Pd/Al$_2$O$_3$ catalyst mass ratio in the range of 100–400.

Catalyst samples were heated to reaction temperatures in a flowing H$_2$–He mixture (5 kPa H$_2$ in He, Praxair, UHP grade, 0.083 K s$^{-1}$, 1.67 cm$^3$ s$^{-1}$) and then treated in He (Praxair UHP grade, 1.67 cm$^3$ s$^{-1}$) for ∼0.2 h. Reactant mixtures consisting of 25% CH$_4$/He (Matheson, Certified Plus grade), 1% CO/He (Praxair, Certified Standard), O$_2$ (Praxair, UHP grade) or 5% O$_2$/He (Praxair, Certified Standard), and He (Praxair, UHP grade) were measured using electronic mass flow controllers (Porter 201). H$_2$O (doubly distilled and deionized) or D$_2$O (Aldrich, 99.9% D) were introduced using a syringe (Hamilton, no. 1005, 5000 μL) at a rate controlled by a syringe pump (Cole Parmer, model 60061) into a heated line (423 K) swept by gaseous reactants. Reactant and product concentrations were measured using a gas chromatograph (Agilent 3000A Micro GC) equipped with modules that contain PorapLOT Q or Mol Sieve 5A columns and thermal conductivity detectors. The reactor was operated in a differential mode, where CH$_4$ conversions were maintained below 4% and for kinetic measurements in Section 3.5 below 0.5%. CH$_4$ turnover rates were determined from effluent CO and CO$_2$ concentrations and O$_2$ chemisorption uptakes, the latter of which provides the total number of exposed Pd atoms available for chemical turnovers.
Reactions of $^{16}$O$_2$—$^{18}$O$_2$, CH$_4$—$^{16}$O$_2$—$^{18}$O$_2$, $^{13}$CH$_4$—$^{12}$CO—O$_2$, CD$_4$—O$_2$, $^{13}$CH$_4$—$^{12}$CO—O$_2$, CD$_4$—H$_2$O—O$_2$, and CH$_4$—D$_2$O—O$_2$ mixtures were carried out in the tubular flow reactor described above by incorporating isotopic compounds (2% $^{18}$O$_2$/He (Icon, 98% $^{18}$O), $^{13}$CH$_4$ (Isotec, 99% $^{13}$C), CD$_4$ (Isotec, 99% D), or D$_2$O (Sigma-Aldrich, >99.9% D)) into the feed mixtures. The isotopic composition of each chemical species in inlet and outlet streams was measured by mass spectrometry (Agilent 6890 and 5973 N). CaSO$_4$ (Drierite) was used to remove water isotopologues before analysis.

3. RESULTS AND DISCUSSION

3.1. Effects of Intrapellet and Bed Dilution on CH$_4$ Conversion Turnover Rates. Reactions of CH$_4$ with O$_2$ on supported Pd clusters form CO$_2$ and H$_2$O almost exclusively at all conditions leading to detectable outlet O$_2$ concentrations (Section 3.2). Sequential reactions of CH$_4$ with CO$_2$ and H$_2$O combustion products form CO (and H$_2$) after O$_2$ depletion. Prevalent exothermic combustion reactions cause severe temperature and concentration gradients within individual catalyst pellets and across the reactor bed in the absence of extensive dilution at the bed and pellet scales, which allows rates to be measured under conditions of strict kinetic control.$^{31,32}$ Measured CH$_4$ consumption turnover rates as a function of O$_2$ pressure are shown in Figure 1. (a) O$_2$ pressure dependence of first-order rate constants ($r_{CH_4}$ (CH$_4$))$^{-1}$, also the reactive CH$_4$ collision probabilities) during CH$_4$—O$_2$ reactions at 873 K and time-on-stream intervals of 0—7.2 ks ($\bigcirc$) and 59.4—63 ks ($\bigcirc$) on a 0.2 wt % Pd/Al$_2$O$_3$ catalyst (21.3 nm mean Pd cluster diameter). Two distinct kinetic regimes are observed, where the rate constants are inversely proportional to ($\blacklozenge$, $\bigcirc$) and independent of ($\blacklozenge$, $\bigcirc$) O$_2$ pressure, respectively. (b) Effects of O$_2$ pressure on fractional CO contents, CO/(CO + CO$_2$), during CH$_4$—O$_2$ reactions at 873 K and time-on-stream intervals of 0—7.2 ks ($\bigcirc$, $\blacklozenge$) and 59.4—63 ks ($\bigcirc$) on a 0.2 wt % Pd/Al$_2$O$_3$ catalyst (21.3 nm mean Pd cluster diameter). Inset: region of low outlet O$_2$ pressure of 0 to 0.05 kPa. (c) O$_2$ pressure dependence of first-order rate constants ($r_{CH_4}$ (CH$_4$))$^{-1}$, also the reactive CH$_4$ collision probabilities) during CH$_4$—O$_2$ reactions at 973 K and time-on-stream intervals of 0—7.2 ks ($\bigcirc$, $\blacklozenge$) and 77.4—82.8 ks ($\times$, $\bigcirc$) on 0.2 wt % Pd/Al$_2$O$_3$ catalyst (21.3 nm mean Pd cluster diameter). Three distinct kinetic regimes are observed, where the rate constants are proportional to ($\times$), inversely proportional to ($\blacklozenge$, $\bigcirc$) and independent of ($\bigcirc$, $\bullet$, $\bigcirc$) O$_2$ pressure. (d) Effects of outlet O$_2$ pressure on fractional CO contents, CO/(CO + CO$_2$), during CH$_4$—O$_2$ reactions at 973 K and time-on-stream intervals of 0—7.2 ks ($\blacklozenge$, $\bigcirc$) and 77.4—82.8 ks ($\times$, $\bigcirc$) on 0.2 wt % Pd/Al$_2$O$_3$ catalyst (21.3 nm mean Pd cluster diameter). Additional data on the fractional CO contents after O$_2$ depletion ($\triangle$) are also included here. Inset: region of low outlet O$_2$ pressure of 0 to 0.05 kPa. 4.85 kPa CH$_4$, 1.57 $\times$ 10$^9$ cm$^3$ (g-atom Pd$_{surface}$)$^{-1}$, 200 SiO$_2$/catalyst intraparticle dilution ratio, 450 quartz/catalyst bed dilution ratio.

Table 1. Intrapellet and Bed Dilution Effects on CH$_4$ Combustion Turnover Rates on a 0.2 wt % Pd/Al$_2$O$_3$ (21.3 nm Mean Pd Cluster Diameter) Catalyst at 973 K

<table>
<thead>
<tr>
<th>catalyst mass (mg)</th>
<th>intrapellet dilution ratio (SiO$_2$/catalyst)$^a$</th>
<th>bed dilution ratio (quartz/catalyst)$^a$</th>
<th>turnover rate (mol CH$<em>4$/(g-atom Pd$</em>{surface}$ s)$^{-1}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>50</td>
<td>150</td>
<td>37</td>
</tr>
<tr>
<td>1.0</td>
<td>50</td>
<td>280</td>
<td>35</td>
</tr>
<tr>
<td>2.5</td>
<td>200</td>
<td>41</td>
<td>41</td>
</tr>
</tbody>
</table>

$^a$ Mass ratio of diluent-to-Pd/Al$_2$O$_3$ catalyst. $^b$ 4.86 kPa CH$_4$, 1.54 kPa O$_2$, 2.08 cm$^3$ s$^{-1}$, time-on-stream = 3.6 ks.
The Journal of Physical Chemistry C

Page 1 of 11

**Figure 2.** O$_2$/CO reactant ratio effects on oxygen selectivity, defined as the ratio of first-order rate constants (also the reactive collision probabilities) for CO and CH$_4$ oxidation (eq 1) during $^{13}$CH$_4$--O$_2$ reactions on a 0.2 wt % Pd/Al$_2$O$_3$ (21.3 nm mean Pd cluster diameter) catalyst at 973 K (4.85 kPa $^{13}$CH$_4$, 0.81 kPa $^{13}$CO, 0.081 to 0.36 kPa O$_2$, 1.57 x 10$^{-5}$ cm$^3$ (s g-atom Pd$_{surface}$)$^{-1}$, 200 SiO$_2$/catalyst intraparticle dilution ratio, 450 quartz/catalyst bed dilution ratio).

**Scheme 1. Proposed Sequence of Elementary Reaction Steps for CH$_4$--O$_2$ Reactions on Supported Pd Clusters**

<table>
<thead>
<tr>
<th>Elementary Step</th>
<th>Rate/Equilibrium Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1.1 O$_2$(g) + * $\rightarrow$ O$_2$*</td>
<td>$k_{f1}$, $k_{i1}$</td>
</tr>
<tr>
<td>Step 1.2 O$_2$* + * $\rightarrow$ 2O*</td>
<td>$k_{f2}$, $k_{i2}$</td>
</tr>
<tr>
<td>Step 2.1 CH$_4$ + O* + H* $\rightarrow$ CH$_3$* + H*</td>
<td>$k_{f3}$, $k_{i3}$</td>
</tr>
<tr>
<td>Step 2.2 CH$_4$ + O* + * $\rightarrow$ CH$_3$* + OH*</td>
<td>$k_{f4}$, $k_{i4}$</td>
</tr>
<tr>
<td>Step 2.3 CH$_4$ = O* + * $\rightarrow$ CH$_3$* + OH*</td>
<td>$k_{f5}$, $k_{i5}$</td>
</tr>
<tr>
<td>Step 3 C* + O* $\rightarrow$ CO* + *</td>
<td>$k_{f6}$, $k_{i6}$</td>
</tr>
<tr>
<td>Step 4 CO* + O* $\rightarrow$ CO$_2$* + *</td>
<td>$k_{f7}$, $k_{i7}$</td>
</tr>
<tr>
<td>Step 5 2OH* $\rightarrow$ H$_2$O* + O*</td>
<td>$K_{H2O}$</td>
</tr>
<tr>
<td>Step 6 H$_2$O* $\rightarrow$ H* + O*</td>
<td>$K_{H2O}$</td>
</tr>
<tr>
<td>Step 7 CO$_2$* $\rightarrow$ CO$_2$ + *</td>
<td>$K_{CO2}$</td>
</tr>
<tr>
<td>Step 8 CO* $\rightarrow$ CO + *</td>
<td>$1/K_{CO}$</td>
</tr>
</tbody>
</table>

* denotes a surface Pd atom; $\rightarrow$, $\rightarrow$, and $\rightarrow$ denote irreversible, reversible, and quasi-equilibrated steps, respectively; $k_{f}$ and $k_{i}$ are the forward and reverse rate coefficients, respectively, and $K$ are the equilibrium constants for the various steps (i denotes the individual steps 1.1 to 8).

This value reflects the reactivity of O* atoms toward CO, if formed via CO$^*$ desorption before subsequent oxidation, for sequential oxidation to form CO$_2$ during the time scale of a CH$_4$ turnover.

O* selectivities were measured using $^{13}$CH$_4$--O$_2$ reagents on 0.2 wt % Pd/Al$_2$O$_3$ (21.3 nm mean Pd cluster diameter) at conditions that led to complete O$_2$ conversion (Figure 2; 973 K, 4.85 kPa $^{13}$CH$_4$, 0.81 kPa $^{13}$CO, 0.081--0.36 kPa O$_2$). O* selectivities were much larger than unity and increased with increasing inlet O$_2$/CO ratios, indicating that CO scavenges O* much more effectively than CH$_4$. The increase in O* selectivities with O$_2$/CO ratios reflects a preference for CO over CH$_4$ oxidation in regions near the reactor inlet, where O$_2$ pressures are higher, and indicates that detectable CO concentrations are unlikely to be observed when O$_2$ is present at any point along the reactor. After O$_2$ depletion, $^{13}$CH$_4$ reacts with the O* species derived from $^{13}$CO$_2$, which is formed in $^{13}$CO oxidation, to form isotopically mixed CO molecules via reforming routes involving C--H bond activation on exposed Pd site pairs (step 2.1, Scheme 1). It also reacts with the O* species derived from the total combustion products in $^{13}$CH$_4$--O$_2$ reactions. These additional reactions contribute to the reactive collision probabilities of $^{13}$CH$_4$ (with O*). Even with these additional contributions, reactive collision probabilities for $^{13}$CH$_4$ (0.9 to 1.3 mol O$_2$ (g-atom Pd$_{surface}$ kPa s)$^{-1}$) were much smaller than for $^{12}$CO (32--1650 mol O$_2$ (g-atom Pd$_{surface}$ kPa s)$^{-1}$) at all O$_2$/CO ratios (0.064 to 2.6; Figure 2).

Next, we examine the mechanistic basis for the observed effects of O$_2$/CO ratios, which determine the O* coverages, on O* selectivities (Figure 2). The O* coverages are given by kinetic coupling between O* removal by reactions with CO (r$_{CO}$) and CH$_4$ (r$_{CH4}$) and O* formation from O$_2$ dissociation (r$_{O2}$). For O* species at pseudo-steady-state

$$r_{O2} = v_{CO}r_{CO} + v_{CH4}r_{CH4}$$  (2)

$v_{CO}$ and $v_{CH4}$ are the respective O$_2$ stoichiometric coefficients ($v_{CO} = 0.5$ and $v_{CH4} = 1.5$ for CH$_4$ conversion to CO and H$_2$O and $v_{CH4} = 2.0$ for CH$_4$ combustion). The large selectivity ratios
observed (>35 for O₂/CO > 0.064, Figure 2) indicate that rCO is much larger than rCH₄. Together with rate and equilibrium constants in Scheme 1, these results give O* coverages as a function of O₂/CO ratio (derivation in Supporting Information, Section 1)

\[
(O^*) \approx \frac{2k_{1af}K_{O_2}^4}{k_{CO,t}K_{CO}} (CO) \tag{3}
\]

where \( k_{CO,t} \) are the equilibrium constants for adsorption of O₂ (\( k_{1af}K_{O_2}^4 \)), step 1.1) and CO (reverse of step 8) and \( k_{1af} \) and \( K_{CO} \) are the rate constants for O₂ dissociation (step 1.2) and CO oxidation (step 4), respectively, as defined in Scheme 1. This equation, taken together with C–H bond dissociation steps that occur preferentially on the \( *\rightarrow* \) site pairs (step 2.1, Scheme 1)²⁷ prevalent at low O* coverages,¹⁹ leads to a linear dependence of O* selectivities on O₂/CO ratios

\[
O^* \text{ selectivity} = 2v_{O^*} \frac{k_{1af}K_{O_2}}{k_{[\rightarrow*]} (CO)} \tag{4}
\]

These measured O* selectivities allow estimates of maximum CO yields (%YCO) by using mole balances (expressed as CO and CH₄ fractions) in plug-flow reactor models and assuming that all CH₄ turnovers lead to CO₂ formation before oxidation to CO (derivation in the Supporting Information, Section 3)

\[
\%Y_{CO} = \left( \frac{y_{CO}}{y_{CH_4}} \right)_{\max} \times 100\%
\]

\[
= \frac{1}{\alpha - 1} \left( \exp \left( -\frac{1}{\alpha} \ln(\alpha) \right) - \exp \left( -\frac{1}{1 - \frac{1}{\alpha}} \ln(1) \right) \right)
\]

\[
\alpha = \frac{k_{CO,t}K_{CO}}{k_{[\rightarrow*]} (CO)} \tag{5}
\]

These equations give 0.1 to 2.7% maximum CO yields for the range of O* selectivities measured in our experiments (36–1300)³⁴ (Figure 2).

Higher CO yields from CH₄–O₂ reactants would require faster oxidation rates for CH₄ than CO, which become possible only at very low O* coverages. These O* coverages are, however, impractical for the reaction stoichiometries (O₂/CH₄ ≈ 0.5) required for practical CH₄ conversions. The much higher reactivity of CO compared with CH₄ (Figure 2), as also found for Pt¹⁹ and Rh thirty catalysts, at all practical O* coverages and O₂/CO ratios renders CO formation via direct partial oxidation pathways infeasible. The O* coverages and O* selectivities toward CO would be even higher with CH₄–O₂ than with CH₄–CO–O₂ reactants, because CH₄ is a much less effective O* scavenger than CO. These conclusions are consistent with the absence of detectable CO levels at all O₂ pressures above 0.04 kPa in the reactor effluent (Figure 1b,d).

3.3. Chemical State of Pd Clusters during Catalytic CH₄–O₂ Reactions. We probe next surface O* coverages on Pd clusters during CH₄–O₂ reactions and confirm that the bulk of Pd clusters remains in the metallic state throughout the reaction measurements reported herein. During catalysis, surfaces of Pd clusters may not be equilibrated with O₂ to O₂ isotopologue formation. The O* coverages and O* selectivities toward CO would be even higher with CH₄–O₂ than with CH₄–CO–O₂ reactants, because CH₄ is a much less effective O* scavenger than CO. These conclusions are consistent with the absence of detectable CO levels at all O₂ pressures above 0.04 kPa in the reactor effluent (Figure 1b,d).

Figure 3. ¹⁶O/¹⁸O isotopologue formation rates measured in ¹⁶O₂–¹⁸O₂ (●) and CH₄–¹⁶O₂–¹⁸O₂ (▲) mixtures and the approach to equilibrium values (☯), which are the ratios of ¹⁶O/¹⁸O isotopologue formation rates in CH₄–¹⁶O₂–¹⁸O₂ and ¹⁶O₂–¹⁸O₂ mixtures, on a 0.2 wt % Pd/Al₂O₃ (213 nm mean Pd cluster diameter) catalyst at 873 K (▲: 4.86 kPa CH₄, 1.57 × 10⁻⁴ cm³ (g atom Pd surface)⁻¹, 200 SiO₂/catalyst intraparticle dilution ratio, 350 quartz/catalyst bed dilution ratio).
rates are proportional to \((O_2)^{1/2}\), suggesting that exchange involves reactions of \(O_4\), with \(O^*\) on \(O^*\)-saturated Pd clusters, as derived and shown experimentally.\(^{20,37}\) \(^{16}O\) isotopologue formation rates for \(CH_1-16O_2-18O_2\) and \(16O_2-18O_2\) mixtures were the same within experimental accuracy at all \(O_2\) pressures \((\gamma = 1.01-1.09;\) Figure 3\), indicating that \(O^*\) is equilibrated with \(O_2(g)\) during \(CH_4-O_2\) reactions at these conditions. \(O^*\) equilibration was also confirmed from \(CH_4\) chemical conversion rates that consume \(O^*\) atoms significantly lower than the \(O^*\) recombination rates measured from oxygen isotopic exchange under all conditions during \(CH_4\) oxidation catalysis on \(O^*\)-saturated surfaces \((2.5 \text{ mol CH}_4\text{ (g-atom Pd)}^{-1} \times 23-39 \text{ mol } ^{16}O^{18}O\text{ (g-atom Pd)}^{-1}) = 4.86 \text{ kPa CH}_4\text{ (873 K)}\). We conclude that oxygen chemical potentials at Pd cluster surfaces during catalysis are equal to those in \((O_2(g))\) for all conditions used to measure the rate data reported in Sections 3.5.37 \((873 K < 6 \text{ kPa CH}_4 < 1.6 \text{ kPa O}_2)\). Therefore, equilibrium \(O_2\) uptakes on Pd clusters (in the absence of \(CH_2\)) rigorously reflect the \(O^*\) coverages during \(CH_4-O_2\) reactions. These uptakes were measured at 873 K and 1–30 kPa \(O_2\) on 2 wt \% \(Pd/Al_2O_3\) \((5.9 \text{ nm mean Pd cluster diameter})\).

Bulk oxidation of small Pd clusters has been shown to occur at lower oxygen chemical potentials than the large clusters used in the rate measurements reported herein \((21.3 \text{ nm mean Pd cluster diameter})\). The smaller Pd clusters \((5.9 \text{ nm mean diameter})\) give constant oxygen uptakes, expressed in \((O/Pd)\) atomic ratios, of 0.18 at \(O_2\) pressures below 7.5 kPa. (See Figure S-1 in the Supporting Information Section 4 for the \(O_2\) uptake as a function of \(O_2\) pressure.) These \(O/Pd\) ratios resemble those expected for saturation \(O^*\) coverages \((the \text{ expected } O/Pd \text{ ratio } = 0.17 \text{ for } 5.9 \text{ nm hemispherical Pd clusters at surface saturation), as they correspond to an atomic ratio of oxygen-to-exposed Pd of 1.06. Above 7.5 kPa, the \(O/Pd\) ratios increased gradually from 0.18 and reached 0.98 at 25 kPa \(O_2\). This increase corresponds to the formation of bulk PdO. These results confirm that small Pd clusters \((5.9 \text{ nm}),\) in spite of their stronger thermodynamic tendency for bulk oxidation,\(^{29}\) retain their metallic bulk at temperatures \((\approx 873 K)\) and \(O_2\) pressures \((\approx 1.6 kPa)\) used here. Larger metallic Pd clusters are expected to convert to PdO at even higher \(O_2\) pressures; thus, Pd clusters of all diameters used in the rate measurements herein must also be in the metallic phase.\(^{29,28}\)

Bulk oxidation of Pd clusters occurs at higher \(O_2\) pressures and forms \(Pd^{2+}\)-\(O^*\) surface sites that are more effective than the \(O^*\)-\(O^*\) sites on metallic Pd clusters for \(C-H\) bond activation.\(^{28}\) The \(Pd/PdO\) phase transition and its kinetic consequences in \(CH_4-O_2\) reactions are addressed in a parallel study at thermodynamic and chemical equilibrium, where oxygen atoms at surfaces and in the bulk of Pd clusters are equilibrated with each other and with \(O_2(g)\).\(^{28}\) Here, we specifically address the elementary steps and their kinetic relevance for \(CH_4\) oxidation over \(O^*\)-covered metallic Pd clusters by keeping oxygen chemical potentials below those required for bulk oxidation \((\approx 7.5 \text{ kPa O}_2, 873 K)\). We show that the reactive \(CH_4\) collision probabilities depend on \(O^*\) coverages in the same manner on Pd and Pt clusters, suggesting that identical kinetically relevant steps and surface site structures are involved and that they evolve with \(O^*\) coverages in a similar manner.

3.4. Reactive \(CH_4\) Collision Probabilities on Pd Metal Clusters. \(CH_4\) conversion turnover rates were measured during initial contact \((0-7.2 \text{ ks})\) of \(Pd/Al_2O_3\) \((0.2 \text{ wt } \%, 21.3 \text{ nm mean cluster diameter})\) with \(CH_4-O_2\) reactants by varying \(O_2\) pressures at a constant \(CH_4\) pressure \((4.85 \text{ kPa})\). Reactive \(CH_4\) collision probabilities are shown in Figure 1a,c as a function of \(O_2\) pressures at 873 and 973 K, respectively. The reactive \(CH_4\) collision probabilities were constant at high \(O_2\) pressures \((>1.1 \text{ and } 1.3 kPa}\) for 873 and 973 K, respectively) but increased as \(O_2\) pressure decreased, as also observed on Pt clusters.\(^{20}\) These trends were interpreted from kinetic and isotopic data and density functional theory calculations on Pt clusters in terms of a transition in the identity of the kinetically relevant step and of the most abundant surface intermediate with changes in \(O^*\) coverages.\(^{20}\) Specifically, kinetically relevant \(C-H\) bond activation steps occur on \(O^*-O^*\) site pairs at high \(O^*\) coverages but benefit from access to vacant sites in \(O^*-O^*\) site pairs as \(O^*\) coverages decrease with decreasing \(O_2\) pressures. The vacant sites can interact with the C atom in \(CH_3\) groups and stabilize \(C-H\) bond activation transition states, causing the observed increase in reactivity on Pd clusters as \(O_2\) pressure decreases, as also found on Pt clusters.\(^{20}\)

Reactive \(CH_4\) collision probabilities did not depend on \(O_2\) pressure above 1.1–1.3 kPa \(O_2\) (Figure 1a,c), because kinetically relevant \(C-H\) bond activation step must use \(O^*-O^*\) site pairs on \(O^*\)-saturated cluster surfaces, a conclusion confirmed by rate dependencies, normal \(CH_4/CD_4\) kinetic isotope effects, and high \(C-H\) bond activation barriers and pre-exponential factors prevalent for \(O^*\) assisted \(C-H\) bond activation steps, as discussed in Section 3.5. As vacant sites emerge with decreasing \(O_2\) pressures, the first-order \(C-H\) bond activation rate constants increased and reached values larger than for similar steps on \(C-H\) site pairs,\(^{38}\) which limit rates for \(CH_4-H_2O/CO_2\) mixtures\(^{27}\) (step 2.1, Scheme 1; Table 2). On Pt cluster surfaces of high \(O^*\) coverages, \(O^*\) atoms vicinal to exposed metal atoms activate \(C-H\) bonds during \(CH_4-O_2\),\(^{19}\) \(C_2H_4-O_2\),\(^{36}\) and \(CH_3OCH_2-O_2\)\(^{39}\) reactions much more efficiently than metal atom site pairs. \(O^*\) abstracts H atoms from \(CH_4\) whereas exposed metal atoms stabilize \(CH_3\) fragments via concerted oxidative addition into the \(C-H\) bond.\(^{20}\) These \(C^*\)-\(O^*\) site pairs are also more reactive than \(O^*\)-\(O^*\) site pairs on both Pd and Pt,\(^{34,56}\) because surface sites because \(CH_3\) fragments interact with open sites \((*)\) more strongly than with \(O^*\) and stabilize the required transition states. Taken together, the trends of first-order rate constants with \(O_2\) pressures in Figure 1 suggest that \(O^*-O^*\) site pairs assist \(C-H\) bond activation much more effectively than the \(C^*\)-\(*)\) or \(O^*\)-\(O^*\) site pairs prevalent in

<table>
<thead>
<tr>
<th>reaction mixture</th>
<th>mean Pd cluster size</th>
<th>first-order rate constant (mol CH_4 (g-atom Pd_surface s kPa))^{-1}</th>
<th>873 K</th>
<th>973 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH_4-O_2)</td>
<td>21.3</td>
<td>34.6(^*)</td>
<td>58.2(^*)</td>
<td></td>
</tr>
<tr>
<td>(CH_4-CO_2)</td>
<td>12.5</td>
<td>4.0(^*)</td>
<td>12.2(^*)</td>
<td></td>
</tr>
<tr>
<td>(CH_4-H_2O)</td>
<td>12.5</td>
<td>4.3(^*)</td>
<td>12.9(^*)</td>
<td></td>
</tr>
<tr>
<td>(CH_4-H_2O_2)</td>
<td>0.2 wt % Pd/Al_2O_3, 0.17 kPa O_2, 3.6 ks time-on-stream, 1.57 x 10^9 cm^3/(s g-atom Pd_surface)^{-1}, 200 SiO_2/catalyst intraparticle dilution ratio, 450 quartz/catalyst bed dilution ratio.</td>
<td>1.6 wt % Pd/Al_2O_3 from ref,(^{37}) see note in ref(^{38}) for the effects of cluster size.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the absence of O$_2$ (in CH$_4$–H$_2$O/CO$_2$ mixtures) or at high O$_2$ pressures, respectively.

At very low O$_2$ pressures, O$_2$ activation becomes the kinetically relevant step on Pt clusters (8.5 nm mean cluster diameter, O$_2$/CH$_4$<0.08, 873 K). In this regime, turnover rates become proportional to O$_2$ pressure and independent of CH$_4$ pressure, and CH$_4$/CD$_4$ isotope effects are not detected. On Pd, this kinetic regime was detected only at high temperatures (973 K) and very low O$_2$ pressures (<0.2 kPa; Figure 1c). This difference between Pd and Pt reflects stronger O*-Pd bonds than O*-Pt bonds (382 vs 354 kJ mol$^{-1}$ DFT calculated values of an isolated O* atom on Pd(111) and Pt(111) surfaces, respectively$^{41}$), making bare surfaces essentially inaccessible before O$_2$ depletion and the regime that O$_2$ dissociation controls rates nearly undetected on Pd clusters.

The reactive CH$_4$ collision probabilities did not change with time on stream at extended times (similar at 32.4–38.0 and 77.4–82.8 ks; Figure 1a,c), but the rate constants and the transition O$_2$ pressure between regimes were smaller than those measured during initial contact to CH$_4$–O$_2$ reactions (0.2–7.2 ks). These changes appear to reflect the densification of O* monolayers, as proposed on Pd(100)$^{42,43}$ and the formation of more stable structures, within which oxygen vacancies ($\gamma$) are less likely to exist. Therefore, turnover rates and rate constants become smaller after densification, and lower O$_2$ pressures are required for vacancies to form in concentrations for O*- sites to contribute to C–H bond activation rates (<0.2 and <0.3 kPa for 873 and 973 K, respectively). These “deactivation” processes do not reflect the coalescence of Pd clusters because larger clusters would have led to lower O* binding energies and higher reactivity (Section 3.7) and to a transition between regimes to occur at higher O$_2$ pressures.

3.5. Rate Equations and Their Mechanistic Interpretations for CH$_4$–O$_2$ Reactions on Oxygen-Saturated Pd Cluster Surfaces. Next, we report kinetic effects of reactant and product concentrations and CH$_4$/CD$_4$ isotope effects at reaction times (>80 ks) and conditions that led to stable rates and to first-order rate constants independent of O$_2$ pressure on Pd/Al$_2$O$_3$ (0.2 wt %, 21.3 nm mean Pd cluster diameter) at low CH$_4$ conversions (<0.5%); H$_2$O and CO$_2$<0.05 kPa at 873 K). CH$_4$ turnover rates ($r_{CH_4}$) increased linearly with CH$_4$ pressure (1.8–5 kPa) but did not depend on O$_2$ pressure (0.4–1.6 kPa; Figures 4a,b) according to the equation

$$r_{CH_4} = k_{app,1}(CH_4)^{1/2}(O_2)^0$$

(7)

in which $k_{app,1}$ is an effective rate constant. This equation describes the rate data on Pd clusters with mean cluster diameters between 4.5 and 22.3 nm.

These rate data (Figure 4) are consistent with the sequence of elementary steps shown in Scheme 1. In this mechanistic proposal, O$_2$ dissociates to form O* species (steps 1.1 and 1.2, Scheme 1), and the resulting O*-O* site pairs activate C–H bonds in CH$_4$ (step 2.3) to form CH$_2$O and OH*. CH$_2$O undergoes sequential H-abstraction and O* insertion (step 3) steps to form CO (step 8) or CO$_2$ (steps 7 and 9). OH$^+$ recombinations forms H$_2$O (steps 5 and 6) and CO readsoption (reverse of step 8) and oxidation to CO$_2$ (steps 4 and 7) complete a catalytic turnover. O$_2$ dissociation steps (steps 1.1 and 1.2) are quasi-equilibrated, confirmed from equal $^{16}$O$^{18}$O isotopologue formation rates measured during catalysis (in CH$_4$–$^{16}$O$_2$–$^{18}$O$_2$) and at oxygen chemical equilibrium (in $^{18}$O$_2$–$^{16}$O$_2$) and their rate ratios ($\eta$) of unity (Section 3.3). CH$_4$/CD$_4$ kinetic isotope effects, measured on the Pd/Al$_2$O$_3$ catalyst (0.2 wt %, 21.3 nm mean Pd cluster diameters) with CH$_4$–O$_2$ and CD$_4$–O$_2$ mixtures 2.01 at 873 K; these values confirm that C–H bond activation is a kinetically relevant step; the linear dependence of rates on CH$_4$ pressure indicates that C–H bond activation occurs on surfaces with active site structures and concentrations that do not depend on the CH$_4$ or O$_2$ pressure. This requires that cluster surfaces be either uncovered or saturated by species derived from CH$_4$ or O$_2$ (CH$_2^*$ and O*, respectively).

Kinetic studies with CH$_4$–H$_2$O/CO$_2$ reactants showed that C* intermediates are present in kinetically detectable coverages on Pd clusters because of strong Pd–C bonds, but such species do not influence CH$_4$–O$_2$ reactions because O$_2$ is a more effective oxidant than H$_2$O and CO$_2$, confirmed from larger CH$_4$ oxidation rates during reactions with O$_2$ than with H$_2$O and CO$_2$ (Table 2). Pd cluster surfaces partially covered with C* from C–H bond activation steps would have led to different $^{16}$O$^{18}$O formation rates with CH$_4$–$^{16}$O$_2$–$^{18}$O$_2$ and $^{16}$O$_2$–$^{18}$O$_2$ mixtures, instead of the equal rates measured (Figure 3). Reactive CH$_4$ collision probabilities and the activation barriers and pre-exponential factors for C–H bond activation in CH$_4$ on
uncovered Pd clusters (step 2.1, Scheme 1) have been previously established using CH$_4$–H$_2$O/CO$_2$ mixtures ($k_{\text{cis}} \approx 4.0$ mol CH$_4$ (g-atom Pd$_{\text{surface}}$ kPa s)$^{-1}$ at 873 K; activation barrier 81–84 kJ mol$^{-1}$; pre-exponential factor $(3-4) \times 10^8$ kPa$^{-1}$ s$^{-1}$; 12.5 nm mean Pd cluster diameter; Table 3),$^{27,38}$ These values were unlike those measured in CH$_4$–O$_2$ reactions (0.53 mol CH$_4$ (g-atom Pd$_{\text{surface}}$ kPa s)$^{-1}$ at 873 K; activation barrier 158 kJ mol$^{-1}$; pre-exponential factor $1.5 \times 10^8$ kPa$^{-1}$ s$^{-1}$; 21.3 nm mean Pd cluster diameter; Table 3), derived from regression fitting of the temperature dependence rate constant data in Figure 5. These distinct kinetic parameters led us to conclude that the active site structures in CH$_4$–O$_2$ and in CH$_4$–H$_2$O/CO$_2$ reactions must be different. In contrast with CH$_4$–H$_2$O/CO$_2$ reactions, Pd cluster surfaces were not uncovered in CH$_4$–O$_2$ reactions but instead saturated with O* atoms, a conclusion consistent with the atomic ratio of oxygen-to-exposed Pd (O*/Pd$_{\text{surface}}$) of near-unity (1.06) over the O$_2$ pressure range (0.5–6.0 kPa, Section 3.3), which determines the oxygen chemical potentials at Pd cluster surfaces used for rate measurements. (See Figure S-1 of the Supporting Information, Section 4.) The apparent rate constant in eq 7, $k_{\text{app,1}}$, thus reflects the elementary rate constant for C–H bond activation on O*–O* site pairs ($k_{\text{O*/O*}}$, step 2.3).

The activation energy (158 kJ mol$^{-1}$) and pre-exponential factor $(1.5 \times 10^8$ kPa$^{-1}$ s$^{-1}$) for C–H bond activation on O*–O* site pairs on Pd/Al$_2$O$_3$ (0.2 wt %, 21.3 nm clusters; Figure 5) are similar to those on Pt clusters (155 kJ mol$^{-1}$ and 2.1 $\times$ 10$^8$ kPa$^{-1}$ s$^{-1}$, 8.5 nm clusters). These activation barriers are similar to DFT-derived C–H bond dissociation barriers on O* saturated Pt(111) (149 kJ mol$^{-1}$)$^{20}$ and Pd(111) (145 kJ mol$^{-1}$)$^{44}$ surfaces and on O* saturated surfaces of cuboctahedral Pt clusters (149 kJ mol$^{-1}$; 201 Pt atoms).$^{20}$ C–H bond activation on O*–O* site pairs involves H-atom abstraction by one O* to form a [CH$_2$•–O*– OH$^+$]$^+$ transition state,$^{20,44}$ in which the O–H$^+$ bond is nearly formed and the CH$_2$• radical-like species interacts weakly with a vicinal O*, as also proposed for C–H bond activation on V-oxide.$^{45,46}$ These unstable CH$_3$ species lead to transition-state energies much higher than those on O*–O* pairs, where CH$_3$ species interact strongly with the * at the transition state.$^{20}$ Weakly held CH$_3$• species retain most of the translational entropy of the CH$_4$ reactants. As a result, activation entropies are much less negative when O*–O* (−12.6 and −9.8 J (mol K)$^{-1}$ for Pd and Pt,$^{20}$ respectively) instead of O*–O* pairs (−97.1 J (mol K)$^{-1}$ for Pt)$^{20}$ are used for C–H bond activation; their values are also much smaller (in negative values) than estimates by assuming the loss of one translational mode upon formation of the transition state from the gas phase CH$_4$ reactant in the framework of transition state theory (−96 J (mol K)$^{-1}$). 3.6. CO$_2$ and H$_2$O Effects on CH$_4$–O$_2$ Reaction Rates. Next, we consider the influences of excess CO$_2$ and H$_2$O products on CH$_4$ conversion turnover rates and their mechanistic implications. The kinetic consequences of excess H$_2$O and CO$_2$ were measured by adding H$_2$O and 12CO$_2$ to CH$_4$–O$_2$ (or 13CH$_4$–O$_2$) reactants. 13CH$_4$ turnover rates were not affected by 12CO$_2$ (6–12.5 kPa, Figure 6) because CO$_2$-derived intermediates ([CO*$_2$] and [CO$_2$]) were present at negligible coverages during steady-state catalysis. CH$_4$ turnover rates decreased markedly when H$_2$O was added (1–10 kPa). Assumptions of competitive OH$^*$ adsorption via quasi-equilibrated H$_2$O adsorption–desorption steps (steps 5 and 6, Scheme 1), together with irreversible C–H bond activation on O*–O* site pairs and quasi-equilibrated O* adsorption–desorption steps, lead to the rate equation below (derivation in Supporting Information, Section 5):

$$r_{\text{CH}_4} = \frac{k_{\text{O*/O*}}(\text{CH}_4)K_{\text{O}_2}(\text{O}_2)}{\sqrt{K_{\text{O}_2}(\text{O}_2)} + \left\{ \frac{[\text{H}_2\text{O}]K_{\text{O}_2}(\text{O}_2)}{K_{\text{H}_2\text{O}}} \right\}^2} \tag{8}$$

This equation is used to describe the rate data in CH$_4$–O$_2$–H$_2$O mixtures (Figure 6) by linear regression analysis with minimization of residuals. Turnover rates decreased more strongly with increasing H$_2$O pressure than indicated by the functional form of eq 8 (Figure 6), and H$_2$O removal led to the partial recovery of
The involvement of OH* (or OD*) species in the kinetically relevant C–H bond dissociation step and the reversibility of this step can be probed in CH$_4$–O$_2$–D$_2$O mixtures where OH* (or OD*) species are prevalent on Pd cluster surfaces. CH$_3$D must form via the microscopic reverse of the C–H bond activation steps (step 2.3, Scheme 1). The reversibility of this step is expressed in terms of the ratio of CH$_3$D$_x$ formation to forward CH$_3$D$_x$ conversion rates; these ratios were measured with CH$_4$–O$_2$–D$_2$O and CD$_4$–O$_2$–H$_2$O mixtures on 0.2 wt % Pd/Al$_2$O$_3$ (21.3 nm mean Pd cluster diameter) at 873 K. As shown in Figure 7, the ratio of CH$_3$D$_x$ formation to forward CH$_4$ or CD$_4$ conversion rates in CH$_4$–D$_2$O–O$_2$ (●) or CD$_4$–H$_2$O–O$_2$ (●) mixtures at 873 K on a 0.2 wt % Pd/Al$_2$O$_3$ (21.3 nm mean Pd cluster diameter) catalyst (4.9 kPa CH$_4$ or CD$_4$, 1.6 kPa O$_2$, 2.35 × 10$^{-8}$ cm$^3$ (s g-atom Pd$_{\text{surface}}$)$^{-1}$, 50 SiO$_2$/catalyst intraparticle dilution ratio, 350 quartz/catalyst interparticle dilution ratio).

The ratio of CH$_3$D formation to forward CH$_4$ conversion rates in CH$_4$–D$_2$O–O$_2$ (●) or CD$_4$–H$_2$O–O$_2$ (●) mixtures reflects the relative rates of CH$_3$* (or CD$_3$*) and OD$^*$ (or OH$^*$) recombination and forward CH$_4$ chemical turnover. These rates were found to be 0.1 and 0.77 in CH$_4$–D$_2$O–O$_2$ and CD$_4$–H$_2$O–O$_2$ mixtures, respectively, and remain unchanged with D$_2$O (or H$_2$O) pressures (2–8 kPa), apparently because the active site structures on Pd cluster surfaces and OD$^*$ (or OH$^*$) coverages do not vary with the D$_2$O (or H$_2$O) pressures, consistent with CH$_4$ turnover rates that remain essentially unaffected by D$_2$O (or H$_2$O) pressure at excess D$_2$O (or H$_2$O) (>4 kPa, Figure 6).

3.7. Effects of Pd Cluster Size and Oxygen Binding Strength on the Rates of C–H Bond Activation Assisted by Oxygen Atom Site Pairs. The average coordination of exposed metal atoms increases with increasing cluster size; such an increase causes chemisorbed species to be more weakly bound on larger than smaller clusters. For CH$_4$–O$_2$ reactions on O$^*$-covered surfaces, these weakly bound O$^*$ atoms would give higher turnover rates on larger clusters, a trend that we confirm from rate data on Pd clusters with 4.5–22.3 nm diameter in this section.

Rate constants for C–H bond activation on O$^*$–O$^*$ site pairs (k(O$^*$–O$^*$)) were measured in the early stages of reactions (0–7.2 ks) on Pd clusters (4.5–22.3 nm; 0.2 wt % Pd/Al$_2$O$_3$ catalysts) at 873 K (Figure 8). C–H bond activation rate constants increased markedly with increasing Pd cluster diameter (Figure 8), as also observed for CH$_4$–O$_2^*$ and CH$_3$H–O$_2^*$ reactions on O$^*$ saturated Pt cluster surfaces. These trends reflect strong effects of oxygen binding energy on its reactivity for kinetically relevant H-abstraction steps and to a lesser extent its ability to weakly stabilize radical-like CH$_3$ fragments at the H-abstraction transition state (step 2.3, Scheme 1). On model Pt clusters, DFT-derived activation barriers for C–H bond dissociation on O$^*$–O$^*$ site pairs decrease with decreasing O$^*$ binding energy and with increasing stability of OH$^*$, which reflects, in turn, the O$^*$ basicity and the ability of O$^*$ to form stronger OH bonds at the transition states.

These effects of O$^*$ binding energy also cause differences in C–H bond activation reactivity between Pt and Pd atoms for a...
given cluster size and average coordination. DFT-derived heats of atomic O* adsorption are 382 and 354 kJ mol\(^{-1}\) for isolated O* chemisorbed on the fcc sites of Pd\((111)\) and Pt\((111)\) surfaces, respectively.\(^{41}\) The weakly bound O* on Pt are more effective for C–H bond activation than on Pd atoms and lead to higher turnover rates for Pt when compared at the same cluster size and average coordination (Figure 8).

When C–H bond activation occurs on O*–* site pairs, O* binding energy influences not only the O* reactivity but also the number of vacancies in O* monolayers; as a result, cluster size influences both turnover rates and the oxygen chemical potential at which O*–* sites become kinetically visible for the transition between kinetic regimes to occur. Figure 9 shows first-order rate constants (for 0–7.2 ks time on stream) as a function of O\(_2\) pressure on samples with Pd clusters of 4.8 and 21.3 nm mean diameters (0.2 wt % Pd/Al\(_2\)O\(_3\); 873 K). The reactivity of the smaller clusters is lower throughout this O\(_2\) pressure range (0.3–1.6 kPa), although large and small clusters exhibit similar O\(_2\) kinetic responses. The shift from O*–O* to O*–* as C–H bond activation sites, indicated by an increase in rate constants with decreasing O\(_2\) pressure, occurs, however, at a lower O\(_2\) pressure on small Pd clusters (∼0.7 kPa on 4.8 nm; ∼1.2 kPa on 21.3 nm). The stronger O* binding on small clusters leads to lower vacancy densities than that on large clusters at each O\(_2\) pressure; as a result, contributions from the more reactive O*–* site pairs become kinetically visible only at lower O\(_2\) pressures on the small clusters. These effects of cluster size on the involvement and reactivity of O*–* site pairs in C–H bond activation are similar to those observed for CH\(_4\) and CH\(_3\)OH oxidation on Pt and CH\(_3\)\(_2\)OCH\(_3\) oxidation on Pt, Pd, and Rh.\(^{48}\) The effects of surface coordination and cluster size on the binding energy of chemisorbed species and on the availability of vacancies are also evident from the lower reactivity of small clusters observed for NO oxidation on Pd,\(^{37}\) for which rates are limited by O\(_2\) activation on O*–* site pairs, and thiophene hydrodesulfurization on Ru\(^{49}\) and Pt\(^{50}\) clusters, for which rates depend on the availability of vacancies on cluster surfaces nearly saturated with chemisorbed sulfur atoms.

4. CONCLUSIONS

Elementary steps and their kinetic relevance during CH\(_4\) reactions with O\(_2\) on metallic Pd clusters were established based on kinetic and isotopic studies under conditions of strict kinetic control, attained by removal of temperature and concentration gradients within pellets and the catalyst bed by extensive site dilutions. H\(_2\)O and CO\(_2\) were formed nearly exclusively at all nonzero O\(_2\)/CH\(_4\) ratios because reactive collision probabilities for CO oxidation are much larger than those for CH\(_4\) oxidation. This difference in reactivity between CO and CH\(_4\) limits the maximum attainable CO yields from direct CH\(_4\) and O\(_2\) reactions at any practical extent of CH\(_4\) conversion.

Reactive CH\(_4\) collision probabilities (also the first-order rate constants) decrease and then reach constant values with increasing oxygen coverages. This trend reflects a transition in the kinetically relevant step from C–H bond activation on O*–* sites to less reactive O*–O* sites. The relative abundance of oxygen atoms and oxygen vacancies, distribution of O*–* and O*–O* pairs on Pd cluster surfaces, and thermodynamic tendency of bulk Pd oxidation during CH\(_4\)–O\(_2\) reactions are set by the prevalent O\(_2\) pressures because O* atoms and O\(_2\)(g) are chemically equilibrated. C–H bond activation step on O*–O* site pairs exhibits high barriers (158 kJ mol\(^{-1}\)) and unusually high pre-exponential factors (1.48 × 10\(^{10}\) kPa\(^{-1}\) s\(^{-1}\)) that are larger than estimates derived from a transition-state theory formalism assuming the loss of a translational degree of freedom in CH\(_4\)(g). These kinetic parameters are common features for C–H bond activation on O* saturated metal surfaces, which proceeds via a loosely bound methyl radical-like transition state. In contrast, oxygen vacancies in O*–* site pairs stabilize the methyl group at the transition state, decreasing the barriers and, in turn, leading to more effective C–H bond activation on O*–* than O*–O* pairs.

Larger clusters with weakly bound O* are more effective for C–H bond activation than smaller clusters. The transition of

**Figure 8.** Cluster size dependence of initial rate constants for C–H bond activation on O*–O* site pairs on Pd (●) and Pt clusters (▲; from ref 20) at 873 K (●: 0.2 wt % Pd/Al\(_2\)O\(_3\); 1.57 × 10\(^{10}\) cm\(^{-3}\) (s g-atom Pd\(_{\text{surface}}\))\(^{-1}\), 200 SiO\(_2\)/catalyst intraparticle dilution ratio, 450 quartz/catalyst interparticle dilution ratio, measured within 7.2 ks after exposure to CH\(_4\)–O\(_2\) feed mixtures; ▲: see ref 20 for specific reaction conditions for CH\(_4\)–O\(_2\) reactions on 0.2 wt % Pt/Al\(_2\)O\(_3\) catalysts).

**Figure 9.** O\(_2\) pressure effects on first-order rate constants ([C\(_4\)H\(_4\)] \((\text{CH}_3)_2\)) during CH\(_4\)–O\(_2\) reactions on 0.2 wt % Pd/Al\(_2\)O\(_3\) catalysts (4.8 (●, ●) and 21.3 nm (●, ▲) mean Pd cluster diameters) at 873 K. Rate constants are inversely proportional to (●, ●) and independent of (▲, ▲) O\(_2\) pressure (0–7.2 ks, 4.85 kPa CH\(_4\)(1.31 to 1.57) × 10\(^{10}\) cm\(^{-3}\) (g-atom Pd\(_{\text{surface}}\))\(^{-1}\), 200 SiO\(_2\)/catalyst intraparticle dilution ratio, 450 quartz/catalyst interparticle dilution ratio).
kinetically relevant step from C—H bond activation on O*—* to O*—O* site pairs at higher O2 pressures on the larger Pd clusters because oxygen vacancies and O*—* pairs are more abundant than on the smaller clusters. Similar effects of O* binding strength are also observed among different metals. Stronger O* binding on Pd than Pt atoms of the same coordination leads to less effective C—H bond activation on the O*—O* pairs on Pd. These effects of O* binding strength on rates appear to be general for oxidation reactions that involve either the O*(CH4 oxidation on Pd; CH4, C2H6, and CH2OCH3 oxidation on Pt) or the oxygen vacancies (NO oxidation on Pt and Pd) in the kinetically relevant steps.

**ASSOCIATED CONTENT**

Supporting Information. Derivation of O*-to-* ratio in 13CH4—13CO—O2 mixtures; derivation of O*-to-* ratio in 13CH4—13CO—O2 mixtures assuming that C—H bond activation occurs on O*—* site pairs; estimation of maximum CO yields from oxygen selectivity values using mole balances in plug-flow reactor; equilibrium oxygen contents of Pd clusters (5.9 nm mean cluster diameter) at 873 K; derivation of rate expression for C—H bond activation on O*—O* site pairs on Pd surfaces nearly saturated with OH* species. This material is available free of charge via the Internet at http://pubs.acs.org.

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**REFERENCES**

(33) In 13CH4—CO—O2 mixtures and under the complete O2 depletion, CH4 can convert to CO and CO with different reaction stoichiometries of O* atoms.
(34) The calculations assume that both CO and CH4 oxidation reactions follow the first-order reaction kinetics.
(38) Elementary rate constants for C—H bond activation on “*” site pairs (step 2.1, Scheme 1) on the 21.3 nm Pd clusters are expected to be lower than the reported values on smaller Pd clusters in ref 27 because the metal sites with larger coordination are less effective for C-H bond activation (see refs 21–24, 26, and 27).
(40) On Pt clusters, this kinetic regime is defined by the O2/CH4 ratio because the O2/CH4 ratio determines the surface O* coverage via kinetic coupling of C—H and O*—O activation steps.
(44) Buda, C.; Neurock M., unpublished results.