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Partial Palladium Oxidation over Various Oxide Supports for a Higher Reactivity of PdO with Respect to CH₄

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role of the contact Pd/support layer in PdO formation is discussed. Computed barriers of CH₄ dissociation related to separate PdO planes over the oxides are compared with oxidation barriers calculated or measured in other works.

1. INTRODUCTION

The greenhouse potential of CH₄ stimulates researchers to look for an effective and economic way toward full oxidation, especially of lean mixtures of CH4. The main problem for practical application of a Pd catalyst for full CH₄ oxidation is Pd deactivation, which requires an optimization of a redox Pd/ PdO cycle for Pd regeneration.^{1,2} An easily oxidized Pd can participate in the cycle above the temperature of PdO decomposition (or a transition temperature between 610 and 720 K depending on conditions and oxide support¹ or at lower value of 563 K without support³) with a small activation barrier of CH₄ dissociation. The low temperature regime is required to minimize the expenses for heating during CH₄ full oxidation. Hence, PdO part is the most effective working component of the redox cycle under such economic requirement.^{1,4} The oxidation activity of Pd/PdO at 300 °C has recently revealed a dependence on reoxidized surface PdO_r measured from CO spectra.⁵ However, the topic remains controversial since the role of Pd as the most active catalyst (in the terms of activation barrier) at low temperature regime below 400 °C has been shown.^{6,7} A kind of compromise between the types of the most active phases was proposed as the PdO(101)/Pd(100) interface⁸ and the undercoordinated Pd sites at the PdO surface.⁹

Realistic wet gas mixtures require to consider the serious complexities appeared from the poisonous effect of water with the formation of $Pd(OH)_2$.¹⁰⁻¹⁴ Wide experimental works in this domain are only partly involved in the Discussion.¹⁴⁻¹⁶ Respective theoretical analysis of the effects produced by water

on the PdO oxide is not yet fully developed, despite of CH₄ oxidation at PdO was the object of detailed theoretical studies within wide exhaustive kinetic schemes (ref 17 and references therein), modeling based on ReaxFF (ref 18 and references therein) as well as at microlevel¹⁹⁻²² with respect to CH₄ dissociation being the limiting stage of its oxidation. This limiting character can be verified by a consequence of calculated barriers of CH_4 - CH_3 - CH_2 - \cdots oxidation,²³ but it was tentatively restricted by high temperatures only on the basis of combined DFT and kinetic modeling at (101) facet.¹⁷ The oxidation activation barrier and/or turnover-of-frequency (TOF) over PdO depend on its form, i.e., on the measure of crystallinity that was shown experimentally,^{24,25} while the importance of the PdO plane was demonstrated mainly theoretically (see also part 3.3 in more details)^{8,20,26} and by two experimental works (see below).^{27,28} The role of different PdO planes in CH₄ oxidation also deserves further study because the surfaces of real PdO NPs consist of different planes.^{11,4} The activation energies over PdO are usually considered to possess intermediate values between pure Pd (the lowest barriers) and oxidized Pd (the highest barriers).

Received: April 28, 2022 **Revised:** July 19, 2022 Published: August 1, 2022



But accepting relatively high barrier $E^{\#} = 0.76$ eV for CH₄ dissociation at Pd(111) the favor activity was for example assigned to PdO(101) with smaller $E^{\#} = 0.64$ eV relative to Pd(111) and oxidized $Pd(O)^*$ with $E^{\#} = 1.51 \text{ eV.}^4$ However, the role of Pd(111) for full CH_4 oxidation was questioned.²⁷ The main fraction of Pd(111) at Al_2O_3 was transformed to Pd(100) during some first redox cycles.²⁷ The 2D squared Pd(100) lattices are less limited for the reciprocal transformations with tetragonal PdO oxide lattice than Pd(111). PdO(101) slab was often studied experimentally and theoretically at Pd(100) support. This facet competes with the PdO(100) one within wide range of O coverage or gas content (CO/O_2) and pressure.^{30–33} Stranski–Krastanov "layer-island" growth mode of PdO(101) was observed experimentally on Pd(100) and confirmed theoretically with respect to Frank-van der Merwe "layer-by-layer" growth. 30,107 Alternatively, the PdO(001)/Pd(001) formation without support was found using surface X-ray diffraction^{32,34,35} at minor O2 pressure. Comparing with PdO deposited at other supports, as-deposited and oxidized Pd/PdO catalysts did not reveal the PdO(101) plane at $Al_2O_3^{27}$ at all or showed their weak reflexes relative to those from PdO(100) and $PdO(110)^{36}$ with the exception of ref 37.

The components of the Me/MeO_x interface for Me = Pdand Pt in the presence of an oxide support can be changed already after the first catalytic cycle.^{21,31} For Pd, this period was however estimated as more prolonged one depending on the support (faster for silica and slower for alumina).^{38,39} The sizes of real PdO nanoparticles (NPs) are usually large enough (relative to a number of unit cells at the NP sides) to suspect a possible influence of support on the formation of PdO species. The increase in activity of Pd/ γ -Al₂O₃^{38,39} or Pd/ δ -Al₂O₃³ with time is hypothetically associated with the modification of PdO in course of many redox cycles by Baldwin and Burch.³⁸ Calcination (accompanied by γ -Al₂O₃ $\rightarrow \delta$ -Al₂O₃ transition), redispersion or particle size of Pd, thermal effects in the catalyst bed were not found to be relevant for the observed catalyst activation with time.^{38,39} Tight relations between the preferable (200) and (220) planes of Pd and respective (400) and (440) planes of PdO were demonstrated by Garbowski et al. over alumina already after the first oxidation cycle in $CH_4/$ O_2 media applying electron microscopy and nanodiffraction.² Similar PdO(110)/Pd(200) and PdO(200)/Pd(220) correlations between Pd and PdO signals were observed using selected area electron diffraction (high-resolution transmission electron microscopy was also involved).36 They were interpreted in favor of topotactic PdO growth as PdO(100)/ Pd(100) on amorphous $\hat{SiO}_2/NaCl$ in \tilde{O}_2 .³⁶ For elucidating a role of any PdO plane, we would like to connect the stability of various PdO planes at different oxide supports with a goal to derive in future an oxide support which stabilizes the most active PdO planes in a selected process, i.e., CH₄ dissociation. The importance of the support selection for CH₄ dissociation barrier was demonstrated by extreme comparison of the barrier at pure PdO(101) (0.52 eV) and one-layer PdO(101) deposited over Pd(100) (1.20 eV).9 One could admit that a strong distortion of the one-layer PdO(101) slab can be the reason for the drastic change in the barrier value. A presence of such PdO(101)/Pd(100) contact was shown experimentally.^{40,41} The experimental data for CH₄ dissociation are apparently not available for different PdO planes so that theory could help to obtain the barriers for the planes which are stable (in the terms of stabilization energy ΔU_1 or surface energy γ)

at an optimized support and then to calculate the barrier value averaged over various PdO planes stabilized under the required conditions.

An additional factor to be considered for slab stabilization is a possible Pd interaction with a support. A possibility to reduce ZrO₂ by Pd was proposed on the basis of the experimentally observed lower $P(O_2)$ pressure for Pd/PdO equilibrium.⁴ Later tetragonal ZrO_2 (t- ZrO_2) reconstruction was supported by computational evidence in favor of lower coordination of internal Zr and O atoms in $t-ZrO_2(100)$ in contact with Pd(100) or Pd(110) slabs.⁴³ A well-known example of catalytic activity depending on the support reduction was shown for V₂O₅/anatase-TiO₂. A drastic loss of catalytic activity during dehydrogenation was discussed for V2O5 upon anatase transformation to rutile.44 One of the possible reasons can be a partial reduction of V_2O_5 deposited at anatase.⁴⁵ The activity of Pt/TiO_2 can be enhanced when mixed TiO_2 phases are used as the support.⁴⁶ More complex influence of $V_2O_5/$ rutile/anatase ratio in the oxidation processes⁴⁷ was assigned to formation the V-O-Ti bonds at the interface after calcination. Some oxides like V_2O_5 and Nb_2O_5 can change the temperature of anatase transformation to rutile and thus to modify the system.⁴⁸ So, one TiO₂ is known by redox transformations and enhanced O transport that will be shortly involved below (please, see the Discussion).

Here, we would like to verify possible influence of the oxide supports on PdO properties during its formation over the support as it was shown earlier for thin Pd slabs.^{43,49,50} In the first part after Computational Aspects, the geometries and charges of the supports and deposited slabs are discussed. Then their relative stabilities are given in the terms of stabilization energies per PdO unit (part 3.1) and surface energy (part 3.2). A discussion is presented after the analysis of the relation between the stability and catalytic activity of different PdO planes, mainly, (100) and (001)/(010) at various supports (part 3.3). In the Discussion, we address a special role of the Pd layer contacting with a support and conserving the total charge between deposited Pd or PdO slabs.

2. COMPUTATIONAL ASPECTS

Plane wave computations with the periodic boundary conditions using traditional PBE⁵¹ functional (including in few cases, zero damping D3,^{52,53} and Becke–Johnson (D3BJ)^{52,53} dispersive corrections⁵⁴ for illustrations) within the projector augmented wave (PAW) method^{55,56} were performed with VASP.^{57,58} The PBE accuracy relative to experimental PdO bulk cell parameters $a_h = 3.0434 \pm 2$ Å and $b_{h} = 5.3363 \pm 4 \text{ Å}^{59}$ is 1.6% and 0.4%, respectively ($a_{b} =$ 3.0920 Å, $b_b = 5.3584$ Å). The energy cutoff was set to 500 eV. The Brillouin zone *k*-sampling was restricted to the Γ -point for the geometry optimization. The Brillouin zone k-sampling was chosen as (442) for the projected density of states (pDOS) calculation for most of the cases ((552) for $Al_{36}O_{64}H_{16}$ and $Al_{48}O_{72}H_{16}$, (332) for rutile TiO₂). The atomic charge density distribution was analyzed using Bader analysis.⁶⁰ The scripts provided by the Transition State Tools for VASP were used to build the initial images for the climbing image nudged elastic band (cNEB) calculations.^{61,62} Vibrational frequencies were calculated using the finite difference method (0.015 Å atomic displacements) as implemented in VASP. For all reactions, the transition states showed a single imaginary frequency corresponding to the reaction path. Zero point energies were



Figure 1. Geometries of (a-c, h, i) PdO(100), (g) PdO(101), (d, e, j) PdO(001), (f) amorphous PdO layers deposited on (a, b) r-TiO₂, $(c, d) Al_{56}O_{80'}$ $(e-g) Al_{36}O_{64}H_{16'}$ (h) m-ZrO₂, and (i, j) a-TiO₂. The side view in part (b) corresponds to the front view in part (a). The atomic colors are given in gray (small spheres), red, gray (large spheres), magenta, green, and cyan light for H, O, Pd, Al, Ti, and Zr, respectively.

neglected for CH_4 because of their small values near 0.02 eV.⁶³ The figures of the 3D structure of the different models were drawn with MOLDRAW 2.0.⁶⁴ Step-by-step control of the CH_4 reactions were realized using wxMacMolPlt.⁶⁵ The support structures of defective $Al_{48}O_{72}H_{16}$ (with undercoordinated Al at the surface), $Al_{43}O_{64}H_8$ (with excessive oxygens at the surface) and nondefective $Al_{36}O_{64}H_{16}$ (Figure le-g) models of γ -Al₂O₃ (100), tetragonal ZrO₂ (100) or t-ZrO₂, rutile form of TiO₂ (100) or r-TiO₂ (Figure 1a,b) were discussed in the precedent works (please, see the part S1 of the Supporting Information for more details and Figure S4).^{49,50,66,67} The new structures of the γ -Al₂O₃(110) (Figure 1c,d, made using the model from ref 68), monoclinic ZrO₂ (100) (Figure 1h),⁶⁹ and the anatase form of TiO_2 (100) (Figure 1i,j)⁷⁰ supports are shortly described below. The (100) slabs of theses oxides corresponds to the realistic models which coexist with the dominant facets $(m-ZrO_2^{71})$ or deviate from the most stable ones within two tens meV/Å² (t-ZrO2(100),⁷² $a-TiO_2^{73}$). These (100) and (110) oriented slabs were constructed from the bulk models using CRYSTAL code.⁷⁴ After that the supercells were created for the proper modeling of CH₄ dissociation to avoid self-interaction, and the vacuum (14 Å) was added above them to avoid the interaction of atoms from the top of the slab with atoms from the bottom of the replicated slab located above. All new γ -Al₂O₃(110), monoclinic ZrO_2 (m-TiO₂), and anatase (a-TiO₂) slabs were constructed without capping H atoms at the lower side where lower coordination was admitted for some fixed atoms (3 for both Ti and O instead of 6 and 3 in bulk anatase, 6 and 2 for Zr and O instead of 8 and 4 in bulk monoclinic ZrO₂, 4 and 2 for Al and O instead of 6/4 and 3 in bulk γ -Al₂O₃(110)) (Figure 1). The geometry of the constructed slab was optimized using VASP. Some deviations from Al/O = 0.6(6)and from Zr/O = 0.5 were admitted for $Al_{56}O_{80}$ and $Al_{14}O_{20}$ (0.7 for two γ -Al₂O₃(110) models) and anatase (0.571), respectively. In the case of γ -Al₂O₃(110) the external planes "C" $(Al_{56}O_{80} \text{ and } Al_{14}O_{20})$ and "D" $(Al_{16}O_{24})$ were used in the terms proposed in ref 75.

Three external planes of PdO were studied. The second case of (010) also occurs at the (100) with another choice of external Pd-layer (Pd-termination) for (010) (contact via mixed Pd/O-layer) instead of usually selected external mixed Pd/O-layer for (100) (contact via Pd-layer). In the work of Rogal et al.⁷⁶ this plane was denoted as PdO(100)-Pd. At the high O_2/CH_4 ratio in the gas mixture no vacancies at the PdO surface (as discussed in refs 4 and 29) were considered.

Because of a frequent formation of amorphous PdO oxide²⁴ at the initial stage of oxidation²⁵ we have also constructed it according to a "melting (3200 K) – quick quenching (300 K)" algorithm⁷⁷ using an initial fragment of 128 atoms (Pd₆₄O₆₄) cut from the tetragonal PdO(001) bulk. Because of the absence of experimental radial distribution functions (RDF) for Pd–X, X = O, Pd, testing of the applied algorithm was realized by modeling amorphous Pd whose RDF was already calculated.^{78,79} We considered the similarity between our data and RDF from independent MD simulations for amorphous Pd^{78,79} as a verification of our algorithm for PdO amorphization. It allowed us to check respective reaction at the amorphous PdO surface (Figure 1f) whose stability was also compared to those of the PdO(001) plane.

3. RESULTS

3.1. Structure and Possible Variants for Joining of the PdO and Oxide Slabs. Unsupported PdO slabs (without a support, with the atoms of the lowest layer frozen, and a vacuum of 14 Å added) were first studied (the upper part of Table 1, Figure 2a-c). As a result, only the lowest Pd-Pd distance of PdO(010) (type 4 in Figure 2b) is slightly contracted (-0.39%) while the upper ones (types 1-3) are elongated (from 1.2 to 5.76%). From a comparison of the distances one can learn that the upper layer of the same (*XYZ*) type, where *XYZ* signifies the crystallographic facet/plane,

Table 1. Changes of the Pd-Pd and Pd-O Distances (%) in
3- or 4-Layer PdO Slabs (Figure 2) Relative to the PdO
Bulk (Pd···Pd = 3.030 Å and Pd-O = 2.0176 Å) without
and with $Al_{36}O_{64}H_{16}$ Support ^{<i>a</i>}

	001	01	.0	100				
N	Pd-O	Pd…Pd	Pd-O	Pd…Pd	IPd-OI			
		no suppor	0)					
1	-4.45	5.76	5.35	-4.37	-1.09*			
2	2.85	1.20	0.14*	5.27	-2.44			
3	0.57	3.90	1.03	1.38	4.03			
4	1.34	-0.39	1.09	6.05	0.54*			
5	1.41		0.97					
6	1.44	2.53 1.40						
7	1.37	-3.45						
8				5.50				
		+ Al ₃₆ O ₆₄ H	I ₁₆ (2-layer Po	dO)				
1	>-5.2°	<6.7 ^c	>6.1 ^c	$\leftarrow 6.2^d$	<-0.1* ^d			
2	_Ь	>-7.8 ^c	>0.02 ^c	>7.5°	<-0.08 ^d			
3	_Ь		>0.02 ^c		>0.08 ^c			
4	>0.7 ^c	<i>b</i> *						
5				Ь				

^{*a*}The distances in the plane which is parallel to the selected one are marked by an asterisk. The numbers of the bond distances increase from the top (no. 1) to the deeper layers (Figure 2). ^{*b*}Both contraction and elongation were obtained. ^{*c*}The lowest boundary. ^{*d*}The highest boundary

relaxes in the same direction in unsupported and deposited slabs. In the case of unsupported slabs, the Pd-Pd distances are shown only for the directions which are perpendicular to the surface (only four Pd-Pd values for (010) and (100)) because the parallel Pd-Pd distances are similar to that of bulk (3.0434 Å). These distances Pd-Pd in deposited PdO are reduced by imposed boundaries from, for example, the $Al_{48}O_{72}H_{16}$ support, up to -7.44% (010), -10.81% (001), and -7.62% (100). The sizes of the selected oxide unit cells are shown in Table S1 of the Supporting Information, which is a complete version of Table 2. The strains in both slab dimensions (Table S3) are stronger for PdO(001) than for PdO(100) and PdO(010) that is in agreement with the worse PdO(001) stabilization. The largest strains for r-TiO₂ explain a strong deformation (Figure 1a,b) and the lowest stabilization energies U_1 for all three PdO facets (Tables 2 and S1), i.e., -10.370, -10.351, -10.078 eV for (100), (010), and (001), respectively, relative to the other systems.

A smaller set of the Pd–Pd and Pd–O data for the deposited models (the lower part of Table 1) is explained by a thinner PdO layer (Figure S1d). Already second Pd–Pd distance in deposited PdO(010) is contracted (-8.77%) whose lowest Pd atoms are in contact with Al₃₆O₆₄H₁₆.

Different variants of joining of PdO and supports were considered. One of the ways is a 90°-rotation of the PdO cell relative to the support (the rotation axis is perpendicular to the support plane). The optimal PdO position above the $Al_{48}O_{72}H_{16}$ model was for example found at less symmetric contact between $Al_{48}O_{72}H_{16}$ (Figure S4c) and PdO(100) with the energies of -11.094 eV/PdO (Figure S2b,d, not shown in Tables 2 and S1) and -11.289 eV/PdO (2 × 1 size is shown in Figure S2a for clarity, Figure S2c, and Tables 2 and S1). The reason for a better joining seems to be a tighter contact between the lowest row of Pd atoms and the undercoordinated Al atoms. The examples of the projected DOS for Pd–Al



Figure 2. Numbering of Pd-O and Pd-Pd distances from the top to bottom (the atoms are fixed in the lowest layer) and of atoms (b) in three (a) (001), (b) (010), (c) (100) slabs. The numbers of O-Pd and Pd-Pd bonds are given in red and black, respectively, in parts (b) and (c). The atomic colors are given in red and gray for O and Pd.

Table 2. Relative PdO Stabilization Energy $\Delta U_1 = U_1(XYZ) - U_1(001)$ per One PdO Pair of Total N Pairs of Deposited Pd_NO_N per Cell with Respect to the Less Stable Plane PdO(001) Obtained through the Total Energies U of Oxide/Support and the Energies U₀ of Support (Table S1), i.e., $U_1 = (U - U_0)/N$ (All in eV)^a

	Al ₃₆ C	D ₆₄ H ₁₆	Al ₄₈	O ₇₂ H ₁₆	Al ₄₃ G	Al ₄₃ O ₆₄ H ₈	
type	$-U_1$	ΔU_1	$-U_1$	ΔU_1	$-U_{1}$	ΔU_1	
001	10.234	0.000	10.663	0.000	10.652	0.000	
010	10.623	-0.389	10.925	-0.262	10.432	0.220	
100	10.724	-0.490	11.289	-0.626	10.956	-0.304	
001	10.097 ^b	0.137 ^b	10.953 ^c	-0.290°	_	_	
	t-Zr ₃₆ C	D ₈₁ H ₁₈	t-Zr ₃₆ O ₈	$_{81}H_{18}^{d}$	r-Ti ₃₆	r-Ti ₃₆ O ₇₂ ^e	
type	$-U_{1}$	ΔU_1	$-U_1$	ΔU_1	$-U_1$	ΔU_1	
001	10.217	0.000	10.839	0.000	10.078	0.000	
010	10.443	-0.226	11.018	-0.179	10.351 ^h	-0.273^{h}	
100	10.690	-0.473	11.287	-0.448	10.370	-0.292	
	<i>m</i> -Zr ₁₆ O ₃₂		m-Z	r ₁₆ O ₃₂	a-Ti	₃₆ O ₆₃	
type	$-U_1$	ΔU_1	$-U_{1}$	ΔU_1	$-U_1$	ΔU_1	
001	10.368 ^f	0.000 ^f	10.482 ^g	0.000 ^g	10.275	0.000	
010	10.488	-0.120	10.630 ^g	-0.263^{g}	10.559	-0.284	
100	10.661	-0.293	10.770 ^g	-0.402^{g}	10.709	-0.434	
	$\mathrm{Al}_{56}\mathrm{O_{80}}^{j}$		Al_{10}	$Al_{16}O_{24}^{k}$		O_{20}^{k}	
type	$-U_{1}$	ΔU_1	$-U_{1}$	ΔU_1	$-U_{1}$	ΔU_1	
001	10.449 ^{<i>i</i>}	0.000	10.456	0.000	10.539	0.000	
010	10.885	-0.436	10.685	-0.229	10.982	-0.443	
100	10.876	-0.427	_	_	_	_	

^{*a*}*XYZ* signifies a plane of PdO, N = 32 except of the cases f–k shown in the footnotes. The abbreviations are used for the oxides: a-TiO₂ and r-TiO₂ for anatase and rutile forms of TiO₂, respectively, t- and m-letters for tetragonal and monoclinic forms of ZrO₂, respectively, Al₄₈O₇₂H₁₆, Al₄₃O₆₄H₈, and Al₃₆O₆₄H₁₆ for γ -Al₂O₃(100) models, and Al₁₄O₂₀, Al₁₆O₂₄, and Al₅₆O₈₀ for γ -Al₂O₃(110) models. Amorphous Pd₆₄O₆₄/Al₃₆O₆₄H₁₆ possesses U = -1440.105 eV, $U_0 = -782.358$ eV (Table S1), so that $U_1 = -10.418$ eV and $\Delta U_1 = -0.184$ eV relative to PdO(001)/Al₃₆O₆₄H₁₆. ^{*b*}O-layer contacts (Figure S2e) instead of the Pd-layer at the (001) plane with -10.234 eV/PdO (Figure S2f). ^{*c*}(100)Pd/O-layer contacts instead of the (010)Pd-layer above (-10.925 eV/PdO). ^{*d*}PBE-D3BJ/PAW. ^{*c*}One PdO(100) type was optimized which held the elements of the crystalline form, while two others, PdO(010) and PdO(001), are strongly destroyed. ^{*f*}N = 18 pairs of PdO. ^{*g*}N = 36. ^{*h*}N = 48 for (100), $U_1 = -10.212$ eV at N = 60 and (100); the data for (010) are not obtained. ^{*i*}N = 40 ^{*j*}N = 48 ^{*k*}N = 12.

(Figure S7a) and Pd–O (Figure S7b–m) contacts including for comparison the O atoms from PdO part (Figure S7b,e,f,i,j) also. One Pd atom can contact with one O atom of the support (Figure S6). The similar shapes below Fermi energy of the DOS peaks of occupied Pd and nearest O atomic orbitals (Figure S7) reveal Pd binding to surface Al and O atoms. Earlier it was shown that the better Pd interaction with γ -Al₂O₃(110C)⁶⁶ than with γ -Al₂O₃(100)⁶⁷ is due to the attainable pair of Al atoms in the first case. The arrows show two bonds (2.492, 2.424 Å) for each undercoordinated Al in the asymmetric model (Figure S2c) and one bond (2.291 Å) only in the symmetric case (Figure S2d). More stable second model (Figure S2a,c) was then used (Tables 3–7). Two different directions deviating by 90° of the PdO(010) deposition were selected over $Al_{56}O_{80}$ and $Al_{14}O_{20}$, mainly due to a limited size of the last model (the models of the same 2D sizes for C and D planes of γ -Al₂O₃(110)⁷⁵ are compared in Figure S5a–c, i.e., 1 × 1 model for $Al_{56}O_{80}$ and 2 × 2 models for $Al_{16}O_{24}$ or $Al_{14}O_{20}$).

Different deformations were observed for PdO(010) and PdO(001) planes deposited over m- ZrO_2 (Figure S3). PdO(010) demonstrates a formation of similar Pd-crests at

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Table 3. Bader Charges (e) of PdO(XYZ) Fragment per UC (with 32 Pairs of PdO Except in Cases c-e), Where XYZ Signifies a Plane, or Pd Fragment per UC, ^{49,66} at Various Slab Oxide Supports Without Defects^{*a*}

		XYZ		
support	001	010	100	Pd ⁴⁹
$t\text{-}Zr_{36}O_{81}H_{18}$	-0.309	-0.592	-0.065	-0.278 , ^h -0.299^{i}
r-Ti ₃₆ O ₇₂	0.354 ^b	-	0.696 ^c	$0.643^{h}_{i} \ 0.958^{i}_{i}$
	0.405 ^d	-	0.438 ^e	_
a-Ti ₃₆ O ₆₃	0.070	-1.879	0.369	_
Al ₃₆ O ₆₄ H ₁₆	0.466	-1.255	0.775	$0.329^{h}, 0.319^{i}$
Al ₄₈ O ₇₂ H ₁₆	-9.936	-5.994	-10.293	-9.596 , ^{<i>h</i>} -9.289^{i}
			-10.518^{f}	$-9.419^{f,i}$
$Al_{43}O_{64}H_8$	2.721	1.920	0.145	$2.768,^{h} 2.730^{i}$
Al ₅₆ O ₈₀	-5.026	0.094	1.471	$-6.126^{j}_{,j} - 5.148^{k}_{,j}$
$Al_{14}O_{20}^{l}$	-1.328	-1.775 ^g	-	_
		$-1.778^{g,f}$		
$Al_{16}O_{24}^{l}$	-0.304	-0.591^{g}	-	-

^{*a*}Anatase and rutile forms of TiO₂, tetragonal form of ZrO₂, Al₁₄O₂₀, Al₁₆O₂₄, and Al₅₆O₈₀ for γ -Al₂O₃(110) models, and three γ -Al₂O₃(100) models without (Al₃₆O₆₄H₁₆) and with surface defects for models (Al₄₈O₇₂H₁₆ with undercoordinated Al at the surface, Al₄₃O₆₄H₈ with excessive O atoms at the surface), all optimized at the PBE/PAW level. ^{*b*}(PdO)₃₂. ^{*c*}(PdO)₄₈. ^{*d*}(PdO)₅₀. ^{*e*}(PdO)₆₀ ^{*f*}Twice as large, 2 × NG, number of the points on the integration grid used to calculate the charges. ^{*g*}Rotated. ^{*h*}2-Layer Pd(100) or Pd₃₆. ^{*i*}4-Layer Pd(100) or Pd₇₂. ^{*j*}Monolayer Pd₂₄ at the most stable configuration; ⁶⁶ ^{*k*}2-Layer Pd₄₈. ⁶⁶ ^{*l*}(PdO)₁₂.

the upper surface irrespective of its thickness (2-, 3-, or 4-PdO layers in Figure S3a-c) with an ordered internal structure. More complex distortion of both external and internal PdO(001) parts of the slab varies with its thickness Figure $S3d_{e}$.

The alternative Pd-, O-, or Pd/O-contacts along the same (XYZ) plane were also tested. The examples of PdO(001) joining via the "Pd-top" (Figure S2e) or "Pd-bottom" (Figure S2f) contacts with $Al_{36}O_{64}H_{16}$ correspond to PdO(001) rotation around the axis which is parallel to the support plane (case "b" in Table 2 and its full variant Table S1). The contacts formed by the $Al_{36}O_{64}H_{16}$ support and PdO(001) slabs yields a difference (Table S1) of 10.097 - 10.234 =-0.137 eV/PdO for the more stable "O-top" configuration (Figure S2f). This difference is smaller in absolute value than the gain of the most stable PdO(100) slab for most of the oxides, i.e., from $-0.626 \text{ eV} (Al_{48}O_{72}H_{16} \text{ in Table 2})$ to -0.292eV (r-Ti₃₆O₇₂ in Table 2). The usual advantage of $PdO(100)^{30,76}$ is only once violated in favor of PdO(010)over $Al_{56}O_{80}$ model, i.e., $\Delta U_1 = -0.439$ eV compared to -0.427 eV for PdO(100).

The larger destabilization ($\Delta U_1 = 0.22 \text{ eV}$) was obtained for PdO(010)-plane contacting with the mixed Pd/O-surface of the Al₄₃O₆₄H₈ model compared to the PdO(010) contacts in two other Al₄₈O₇₂H₁₆ and Al₃₆O₆₄H₁₆ models (Table 2). The lower energy is a consequence of a high O concentration at both PdO and Al₄₃O₆₄H₈ oxides (Figure S4b).

As we mentioned above, the PdO(010) plane is identical with the case of Pd/O-layer at the PdO(100) surface. But the difference obtained at the Al₄₈O₇₂H₁₆ model between the PdO via (010) plane ($U_1 = -0.262$ eV in Table 2) and the Pd/O-layer via the (100) plane (in case "b" in Table 2), both of them should correspond to Figure 2b) takes around 0.028 eV = 0.64 kcal/mol (0.290 - 0.262 = 0.028 eV) from two independent models, thus characterizing the error of our calculations.

3.1.1. Bader Charge Analysis. The main issue of the Bader charge comparison is their minor variation between the isolated and deposited PdO slabs (Table 4) despite of the drastic deviation of the parallel Pd–Pd distances (3.030–2.805 Å). This independence of the charges in the upper PdO layer

Table 4. Bader Charges (e) and Distances (Å) of Isolated Slabs PdO(010) and Deposited on $Al_{36}O_{64}H_{16}$ (Figure S1d)^{*a*}

PdO(010)	$PdO(010)/Al_{36}O_{64}H_{16}$			
Pd90	0.360	Pd156	0.349		
Pd78	0.406	Pd164	0.349		
Pd95	0.843	Pd155	0.801		
Pd83	0.843	Pd163	0.840		
O42	-0.792	O108	-0.776		
O30	-0.792	O100	-0.778		
Pd90-Pd78	3.030	Pd156-Pd164	2.805		
Pd90-Pd88 ^b	3.205	Pd156-Pd154 ^c	3.232		

^{*a*}The atomic notations are in Figure 2 for the left column while the atoms in the right column exactly correspond to those in the left one. ^{*b*}Distance of the type 1 in Figure 2b. ^cPositions of the Pd, O atoms in the deposited slab correspond to those in unsupported PdO(010) slab (Figure 2b).

resembles the insensitivity of the Bader⁴⁹ and Mulliken- or Löwdin-type⁸⁰ Pd charges in deposited slabs starting from the second Pd layer which is not in a contact with a support. More evidence about the weak influence of the PdO geometry on the atomic charges of remote layers can be obtained from Table 3. We remind that the lowest PdO(100) and PdO(001) planes correspond to the pure Pd-contacts while that for PdO(010) involves both Pd and O atoms (Figure S1d). The numbers of the lowest 3-coordinated Pd atoms (counting O neighbors only) in the lowest layer (contacting ones) deviate however as much as twice (16 Pd from PdO(001), Figure S1e, and 8 Pd from PdO(100), Figure S2b,d). Hence the PdO(001)/support contact zones are the most similar to Pd(100)/support where 16-18 atoms were used.⁴⁹ As a result the total Bader charge of the PdO(001) fragment approaches better the one of a Pd fragment of the Pd(100)/support compared to that of PdO(010) or PdO(100) with the exception of $r-Ti_{36}O_{72}$ (Table 3). In the last case the Bader charge of PdO(100)layer matches better the Pd(100) charge after the contact with r-Ti₃₆O₇₂ support (Table 3). It demonstrates a dominant role

Table 5. Surface Energy γ (meV/Å²) of PdO(XYZ) without Support⁷⁶ (3rd column from the left), Modeled over Pd(100)³⁰ (4th column from the left), Calculated Herein as $\gamma = (U_1 + 11.019) \times N/(a \times b)$, Where -11.019 eV/PdO is the PBE/PAW Stabilization Energy in Bulk PdO^{*a*}

				this work					
		litera	ture	γ -Al ₂ O ₃					
(XYZ)	termination	ref 76	ref 30 ^b	(110)	(100)	$a-TiO_2$	r-TiO ₂	t-ZrO ₂ ^c	m-ZrO ₂ ^c
(100)	Pd, O	33, 18 ^j	72	38	75	77	110, ^g 169, ^h 255 ⁱ	86	83
$(010)^{d}$	Pd	119	-	36,10, ^e 88 ^f	101	114	-	150	129
(001)	0	119	167	152, 128, ^e 150 ^f	200	185	159 ^g	210	179
(101)	O-Pd ₂ -O	57, 52 ^j	121	-	66	_	_	_	_

^{*a*}The energy U_1 values (Table 2) per PdO unit of *N* pairs in Pd_NO_N deposited per cell and (*a*, *b*) cell parameters are given in Table S1 of the Supporting Information for other supports: Al₅₆O₈₀ (Figure S5a), Al₃₆O₆₄H₁₆, anatase or a-TiO₂ (Ti₃₆O₆₃), rutile or r-TiO₂ (Ti₃₆O₇₂), tetragonal ZrO₂ or t-ZrO₂ (Zr₃₆O₈₁H₁₈), and monoclinic ZrO₂ or m-ZrO₂ (Zr₁₆O₃₂). The upper termination (contact with CH₄) signifies the types of atoms at the upper PdO layer. Amorphous Pd₆₄O₆₄/Al₃₆O₆₄H₁₆ possesses $U_1 = -10.418$ eV (Tables 3 and S1), so that respective points (shown in Figure 3a at $\Delta U_1 = -0.184$ eV) with $\gamma = 305.7$ meV/Å² are omitted in Figure 3b. ^{*b*}Smaller values from ref 30 correspond to "uncompressed" PdO (15, 82, and 63 meV/Å²) for (100), (001), and (101), respectively. ^{*c*}Smaller values of 79, 118, 108 meV/Å² correspond to (100), (010), (001), respectively, at N = 24, 24, and 18. ^{*d*}Denoted as "PdO(100)-Pd" in Table 1 of ref 76. ^{*e*}Al₁₄O₂₀, Figure S5b. ^{*f*}Al₁₆O₂₄, Figure S5c. ^{*g*}N = 32. ^{*h*}N = 48. ^{*i*}N = 60. ^{*j*}Reference 105.

of contact Pd layer in PdO for the total charge of the slab as well as it was observed for Pd slab.⁴⁹ The closeness of Pd charges of the lowest contacting Pd layer between Pd and PdO could signify a conservation of total charge in the course of Pd reoxidation. According to refs 25 and 81, initial Pd oxidation is driven by electric-field within the Cabrera–Mott mechanism, while the subsequent PdO formation is likely controlled by O diffusion through already deposited PdO.²⁵ The similar charges at PdO and Pd slabs (Table 3) allow avoiding an electrostatic barrier at final oxidation step. Possibly, relative easiness of atomic Pd displacements at the contact surface allows to partly reorient the bonds accordingly the support structure thus creating a precursor of bulk oxide.

3.2. Surface Energy of Deposited PdO. Relative stability of the PdO(*XYZ*) slabs is often expressed via the surface energy: 30,76

$$\gamma(XYZ) = (U_1(XYZ) + 11.019) \times N/(a \times b)$$
(1)

Here U_1 is the energy value per one deposited PdO pair of total N pairs of deposited Pd_NO_N, -11.019 eV/PdO is the PBE/PAW stabilization energy in bulk PdO (-11.613 eV/PdO at the PBE-D3/PAW level), and (*a*, *b*) cell parameters are given in Table S1 of the Supporting Information.

We found some data about PdO(101) stabilized mainly at Pd,^{9,30,40,82} in one case at Al₂O₃,³⁷ and possibly over amorphous SiO₂/NaCl(001) upon pure O₂ oxidation³⁶ (see Discussion) so that the $\gamma(101)$ value was also calculated for comparison, being the lowest one (66 meV/Å²) throughout all other PdO planes over Al₃₆O₆₄H₁₆ (Table 5). One should note a coherence $\gamma(100) < \gamma(101) < \gamma(001)$ between results from refs 76 and 30, both obtained with PBE. This γ -sequence⁷⁶ was obtained with full potential LAPW using WIEN2K⁸³ instead of pseudopotential PAW and VASP^{57,58} used in ref 30, so that a nearly constant γ -shift between the data^{30,76} for same (*XYZ*) planes (Table 5) might be the result of the different computational levels. One should emphasize inverted $\gamma(100) > \gamma(101)$ over Al₃₆O₆₄H₁₆ compared to the results for multilayer PdO without support⁷⁶ or deposited over Pd(100).⁷⁶

Together with Table 5 more $\gamma(XYZ)$ -comparison with the data from ref 76 can be done at low temperature limit for the heat of formation of PdO (T = 0 K, P = 0 bar). The $\Delta U_1 = 0.364$ eV/PdO between PdO(100) or PdO(010) at

Al₄₈O₇₂H₁₆ (part 3.1, Table 2) results in the $\gamma(100)$ difference of 93 meV/Å², being close to 88 meV/Å² according to Figure 2 of ref 76. From the same Figure 2⁷⁶ one can obtain $\Delta\gamma(001) =$ 37 meV/Å² difference between Pd- or O-termination of PdO(001) relative to 35 meV/Å² herein from $\Delta U_1 = 0.137$ eV/PdO at Al₃₆O₆₄H₁₆ (part 3.1, Table 2).

Regarding surface energies calculated in this work for various supports, the common feature with previous results^{30,76} is the same ratio between the $\gamma(100) < \gamma(001)$ planes which are the most important for all our oxide supports (Table 5) in agreement with $|U_1(100)| > |U_1(010)| > |U_1(001)|$ on the basis of relative energies (Table 2). This sequence is justified in the case of limited adaptability of PdO to the rutile (or $r-Ti_{36}O_{72}$) surface (Figure 1a, b). R-Ti₃₆O₇₂ allows a formation of a crude PdO(100) slab in which additional contraction leads to the shorter Pd…Pd bonds being absent for PdO(100) on other supports (gray sticks shown by arrows in Figure 1a,b). Both criterions (γ and U_1) show on the same less stable PdO(100)/ r-Ti₃₆O₇₂ object relative to other supports, i.e., the lowest | $U_1(100)$ = 10.370 eV (Table 2) and highest $\gamma(100)$ = 110 meV/Å² (Table 5). The attempts to add more layers (at N =48 and 60 for Pd_NO_N) over did not improve the stability (Tables 2 and 5). It is instructive that external (visual) "accuracy" of the optimized slab cannot serve for the crude conclusion about relative stability. Other PdO(010) and PdO(001) slabs are totally distorted (not shown) and obtained in nearly "amorphous" form. Nevertheless, their increases of the surface energy are moderate ($\gamma = 169$ and 159 meV/Å², Table 5) compared to more accurate geometry of the $Pd(001)/Al_{36}O_{64}H_{16}$ slabs with $\gamma = 200 \text{ meV/Å}^2$ (Figure 1f). Respectively, $\gamma(001) = 159 \text{ meV}/\text{Å}^2$ corresponds to minimum | $U_1(001)$ = 10.078 eV (in absolute value) obtained throughout all the crystalline systems. Despite the geometry reconstruction, the Bader charge distribution in PdO does not vary much (Tables 3 and 4).

Two cases of $\gamma < 0$ are obtained for the PdO(100) over defective Al₄₈O₇₂H₁₆ slab due to a strong interaction (PBE level) and tetragonal ZrO₂ (PBE-D3BJ level, not shown in Figure 3b). For the latter, a strong relaxation effect in some t-ZrO₂ layers was noted as the source of additional energy gain in the contact with both Pd(100) or Pd(110) slabs⁴³ that was also observed due to PdO(100).



Figure 3. Activation energy $E^{\#}$ of CH₄ dissociation versus the (a) relative stabilization energy $\Delta U_1 = -U_1(XYZ) + U_1(001)$ per one PdO pair of total *N* pairs of deposited PdO with respect to the less stable plane PdO(001), where $U_1 = (U - U_0)/N$ per PdO pair (all in eV), *XYZ* signifies a plane of PdO, total energies *U*₀ and energies *U*₀ of support only are given in Table S1, and *N* = 32 except in cases f–k shown in the footnotes of Tables 2 and S1 and (b) the surface energy $\gamma(XYZ) = (U_1(XYZ) + 11.019) \times N/(a \times b)$, where -11.019 eV/PdO is the PBE/PAW stabilization energy per deposited PdO unit in bulk PdO and (*a*, *b*) cell parameters are given in Table S1 of the Supporting Information. The sign notations are used for the oxides: triangles (γ -Al₂O₃, upper filled for Al₄₃O₆₄H₈, right filled for amorphous PdO/Al₃₆O₆₄H₁₆, left filled for PdO(101)/Al₃₆O₆₄H₁₆, empty for Al₄₈O₇₂H₁₆, filled for Al₅₆O₈₀), stars (TiO₂, empty for anatase, filled for rutile), pentagons (ZrO₂, filled for m-ZrO₂, open for t-ZrO₂), and circles (no support).

3.3. Stabilization of Deposited PdO versus CH₄ Reactivity. In order to illustrate a correlation between stabilization and reactivity toward dissociation of CH₄ over PdO deposited *via* its different planes, we calculated the barriers and related the lowest barriers only for the PdO(*XYZ*) plane/support pairs with respective stability ΔU_1 (Figure 3a). The latter was scaled relative to the less stable PdO(001) plane. The points with higher barriers for the same plane/ support pair were not displayed in the Figure 3a, for example, the higher 1.06 eV at PdO(001)/ γ -Al₂O₃(100) (0.70 eV at the PBE-D3 level) instead of 0.62 eV. Between the three reaction routes over Pd/O-terminated PdO(100)/ γ -Al₂O₃(110), we used the route with the lowest barrier value which corresponds to the CH₃ and H reacted with two O atoms of neighboring rows at the Al₂O₃(110) surface (Figure S1a) instead of two alternative reactions (Figure S1b,c). The typical products of CH_4 dissociation over other PdO planes are shown in Figure S1d (PdO(010)) and Figure S1e (PdO(001)).

The maximum number of the $E^{\#}$ data (8 in the ellipse shown by dashed line in Figure 3a,b) was obtained at the most stable (100) facet. It is worth noting that drastically different PdO(100) geometries after such a growing (Figure 1) lead to wide $E^{\#}$ variation for one plane, as from 1.01 eV (Al₅₆O₈₀) to 1.40 eV (m-ZrO₂). The variation of the activation barrier at the same PdO(100) or PdO(010) slabs deposited over a series of oxides covers wide intervals of 1.01–1.40 or 0.45–0.98 eV, respectively, at the same computational level (Figure 3a). These large widths illustrate an importance of the support selection that was earlier shown by drastic difference between

Table 6. Activation Barriers of CH_4 Dissociation Calculated at Different PdO Planes and the Amorphous $Pd_{64}O_{64}$ Model (a-PdO) Using the PBE Level with the VASP Code^{*a*}

plane	$(100)\gamma$ -Al ₂ O ₃ (Al ₄₈ O ₇₂ H ₁₆)	$a-TiO_2$	$r-TiO_2$	m - ZrO_2	$t-ZrO_2$	no support	other calculated data
(100)	1.08, 1.13, ^b 1.01 ^d	1.34	1.22	1.07	1.40	1.26	$1.22,^{f} 1.58,^{k} 1.63,^{k} 1.51,^{e} 1.17,^{g} 0.93,^{g} 1.08,^{n} 1.22,^{o} 0.77^{s}$
(010)	0.67, 0.98 ^b	0.84	-	0.45	_	0.46	-
(001) ^r	$0.62, 0.56^d$	-	-	-	_	_	0.20 ^g
(101)	0.75 ^c	_	-	-	_		$0.50^{f}_{i} 0.67^{h}_{i} 0.79^{i}_{i} 0.57^{j}_{i} 0.52/1.70^{o_{i}p}_{i}, 1.20/1.62^{o_{i}p,q}_{i}, 0.68^{s}_{i} 0.66^{s,t}_{i}$
(110)	-	_	-	-	_	_	$1.36^{e}, 0.47^{g}$
a-PdO	1.38 ^c ,1.45 ^c	_	-	-	_	-	$1.30, 1.66^{m}$

^{*a*}For the different upper boundaries for electron kinetic energy please see in the text of part 3.4 from respective references where available). Experimental data²⁴ are available for amorphous a-Pd₆₄O₆₄ only (see *l*, *m* footnotes). ^{*b*}Al₄₃O₆₄H₈. ^{*c*}Al₃₆O₆₄H₁₆. ^{*d*}Al₅₆O₈₀. ^{*e*}PW91.²⁶ ^{*f*}GPAW code.⁹ ^{*s*}SIESTA code.²⁰ ^{*h*}Reference 19. ^{*i*}Reference 29. ^{*j*}PBE-D3.²¹ ^{*k*}CASTEP code with PW91.²² ^{*l*}Experimental data (±0.16 eV) for CH₄ oxidation over PdO obtained from Pd foil or Pd(100).²⁴ ^{*m*}Experimental data (±0.21 eV) for CH₄ oxidation over PdO obtained from Pd(110).²⁴ ^{*n*}DFT+U with VASP.¹⁰⁶ ^{*o*}Reference 8. ^{*p*}Two-step process. ^{*q*}At the Pd(100) support. ^{*r*}A small quantity of the points with the PdO(001) is explained by its nonstable character and destroyed geometry at other supports. ^{*s*}Reference 28. ^{*t*}Bilayer (101) slab.

barriers of 0.50 eV at pure PdO(101) and 0.98 eV for one-layer PdO(101) deposited over Pd(100).⁹

As demonstrated in Figure 3a, the ΔU_1 values are approximately inversely proportional to reactivity. Even the defective Al₄₃O₆₄H₈ model obeys this trend. The presence of O atoms at the PdO(010) plane contacting with the excessive Ocovered upper side of the $Al_{43}O_{64}H_8$ slab results in a worse relative stability and a unique point $|\Delta U_1(010)| < |\Delta U_1(001)|$ (Figure 3a). Close ΔU_1 values for different planes signify probable parallel formation of both planes. Selecting an oxide with the close ΔU_1 values of the planes increases the probability of highly active support toward CH_4 (Figure 3a). The most drastic slopes of the lines connecting the $(\Delta U_1, E^{\#})$ points for different planes like the "No support" and m-ZrO₂ cases in Figure 3a reveal the best candidates at that condition if any of the planes is active enough. The ΔU_1 differences between PdO(100) and PdO(010) are minor for both the nondefective γ -Al₂O₃(100) and γ -Al₂O₃(110) planes. It takes around of 0.01 eV = 0.2 kcal/mol on γ -Al₂O₃(100) (between -0.490 and -0.389 eV in Table 2) and 0.01 eV = 0.02 kcal/ mol on γ -Al₂O₃(110) (between $\Delta U_1 = -0.427$ and -0.436eV). The respective differences of surface energies between PdO(100) and PdO(010) are also minimal at γ -Al₂O₃(100) $(101 - 75 = 26 \text{ meV}/\text{Å}^2 \text{ in Table 5}) \text{ and } \gamma \text{-Al}_2\text{O}_3(110) (36 - 75) \text{ meV}/\text{Å}^2 \text{ in Table 5})$ $38 = -2 \text{ meV/Å}^2$ planes. The minor differences in γ and ΔU_1 between PdO(100) and PdO(010) for all important planes of γ -Al₂O₃ are the sign of its advantageous activity compared to various ZrO₂ and TiO₂ forms. Similarly, regarding the less stable D-plane of γ -Al₂O₃(110) (for Al₁₆O₂₄) with higher γ = 88 meV/Å² compared to that for C-plane ($\gamma = 10$ and 36 meV/Å² for Al₁₄O₂₀ and Al₅₆O₈₀, respectively, in Table 5), one could admit better activities of the D-plane. Unfortunately, only a part of the reactions was modeled properly.

The increase of $E^{\#}$ barriers with a lower surface energy $\gamma(1)$ of the slabs (Figure 3b) is shown in the " $E^{\#} - \gamma$ " coordinates.¹⁰⁸ The slopes of approximate lines, which could be drawn through two or three " $E^{\#} - \gamma$ " points for the same support, are in the same ratio as in the " $E^{\#} - \Delta U_1$ " coordinates. The higher the slope, the higher the probability to obtain planes with elevated activity in the CH₄ dissociation. If the data for different PdO(100), PdO(010), and PdO(001) surfaces are well grouped in the " $E^{\#} - \Delta U_1$ " coordinates (with the exception of one PdO(010)/Al₄₃O₆₄H₈ point in Figure 3a), the " $E^{\#} - \gamma$ " pairs for PdO(001), PdO(101), and PdO(010) are mixed in a wider range of the γ -values for different supports. Within all the range the data for both types

of the coordinates are pretty similar; i.e., the $E^{\#}$ barriers increase either with the smaller surface energy γ (Figure 3b) or with a higher (in absolute value) relative stability ΔU_1 (Figure 3a).

The model of amorphous $PdO/Al_{36}O_{64}H_{16}$ (Figure 1f) led to the $E^{\#}$ values around 1.4 eV (Table 6 and right filled triangles in Figure 3a) which are in reasonable agreement with those obtained by oxidation of a series of various Pd planes, i.e., from 1.30 ± 0.16 eV (PdO from Pd foil and Pd(100)) to 1.66 ± 0.21 eV (PdO from Pd(110)).²⁴

3.4. Comparison with Other Calculated Barriers of **CH**₄ **Oxidation.** Both relative stability of different PdO planes without a support (expressed via γ or ΔU_1 in Figure 3) and their reactivity with respect to CH4 vary after deposition over various oxides (expressed via $E^{\#}$) (Tables 5 and 6). Our PBE/ PAW value 1.26 eV for such PdO(100) model is within the range of earlier estimations with various methods from 0.93²⁰ to 1.63 eV,²² which is, however, too wide. The PdO(101) was mainly stabilized at metallic supports, ^{9,30,40,82} but its formation at the oxide supports was recorded only once.³⁶ One reaction at PdO(101)/Al₃₆O₆₄H₁₆ (Figure 3) was successfully calculated and showed higher activity $E^{\#} = 0.75$ eV than of the (100) plane together with the comparable surface energy ($\gamma =$ 66 meV/Å² in Table 5). However, this model is less stable than both PdO(100) and PdO(010) orientations on the $Al_{56}O_{80}$ slab (see γ values in Table 5). A series of the active sites at the PdO(101)/Pd(100) interface showed higher barriers (from 0.79 to 1.30 eV) compared to the bulk surface of Pd(100)(0.66 eV) in the same PBE/PAW calculations⁸ with the GPAW code.⁸⁴ The moderate (from +0.05 to -0.41 eV) and high exothermic (-1.09 eV) heats of the dissociation at the PdO(101)/Pd(100) interface and the surface of PdO(100)bulk, respectively, show its thermodynamic advantage relative to that at Pd(100) (endothermic effect of 0.34 eV).

The calculated $E^{\#}$ values can be compared with the results obtained with SIESTA²⁰ where a different method for calculating dissociation barriers was used (Table 6). It gave similar $E^{\#}$ values for PdO(100) (0.93, 1.17 eV) but the smaller value of 0.2 eV for PdO(001) (to compare with higher $E^{\#}$ values of 0.56 eV for PdO(001) at (110) γ -Al₂O₃ in Figure 3). For the other PdO planes intermediate $E^{\#}$ values were computed as 0.47 eV for PdO(110) with SIESTA²⁰ and 0.67 eV,¹⁹ 0.64 eV²⁹ (both with PBE), 0.57 eV (PBE-D3)²¹ for PdO(101) with VASP. CASTEP at the PW91 level (the lower cutoff for kinetic energy was 340 eV²² instead of 500 eV herein) produced higher $E^{\#}$ values of 1.58 and 1.63 eV for two different TS geometries over PdO(100) (Table 6). The barrier for CH₃ migration 1.05 eV from Pd to the O neighbor was also higher at the PW91 (340 eV) level²² instead of 0.98 eV (with PBE and 500 eV) herein over PdO(100)/Al₄₃O₆₄H₈. For comparison, VASP at the PW91 level (cutoff of 400 eV) led to smaller barriers of 1.51 and 1.36 eV for PdO(100) and PdO(110).²⁶ A later PBE result with VASP (no data about upper electron kinetic energy limit) gave the barriers of 1.22 and 0.50 eV for PdO(100) and PdO(101) without support.²⁶ The last difference at Pd(100) support (0.72 eV) is essentially larger than the ~0.34 eV obtained herein at two models of γ -Al₂O₃(100), i.e., PdO(100)/Al₄₈O₇₂H₁₆ and PdO(101)/ Al₃₆O₆₄H₁₆ (shown by horizontal dot-dot-dashed lines in Figure 3b).

4. DISCUSSION

Alternative views on the role of Pd/PdO boundary are widely presented in the literature. One of the earlier hypotheses interprets an advantage of Pd/PdO coexistence due to an easy CH₄ dissociation at the Pd particles with the following migration of the H and CH_x (x = 1-3) species to the Pd/PdO boundary.^{25,85} A delay of the Pd segregation after reduction of PdO by CH₄ was proposed to be the reason for induction period before the quick stage of PdO reduction.²⁵ The absence of Pd phase (and of Pd/PdO as well) hinders the PdO reduction after an addition of La and Ba cations which form oxides and thus bind the Pd species.⁸⁶

The highest CH₄ conversion in a series of alternating reduction/oxidation periods at the beginning of the cycle without O_2 addition (CH₄ only) was assigned to the appearance of the mixed Pd/PdO sites after reduction of oxidized Pd.¹⁰ The quicker Pd oxidation of the catalyst activation was connected with the poor Pt content in a Pd/Pt alloy.⁸⁷ As a result, a lower temperature of CH₄ oxidation was obtained at an oxidation of the Pd/Pt catalyst compared to that while reducing at the absence of the "core-shell" effect in both the cases.⁸⁷ Another point of view about the importance of the Pd/PdO boundary is suggested in ref 88 addressing to the change of electronic state or surface structure of PdO/ Al_2O_3 in the contact with Pd⁰. This change should result in much lower barrier of C-H splitting in the reaction with both Pd^{2+} and Pd^{0} (by as much as 7.6 times smaller) instead of CH_4 oxidation at one Pd^{2+} only.⁸⁸ Theoretical⁶⁷ and experimental⁸⁹ pro arguments could be given. A similar easier C-H splitting was modeled theoretically at two Pd atoms of one Pd monolayer deposited at the γ -Al₂O₃(100) compared to Pd bulk presented by a 4-layer slab at the PBE-D3 level.⁶⁷ The barrier of CH₄ oxidation declines from 0.56 to 0.19 eV for the reaction at two Pd atoms with opposite Bader Pd charges of -0.224 and 0.104 e (in non-spin-polarized approximation or -0.221 and 0.132 e in spin-polarized approximation) induced by Al or O atoms of the γ -Al₂O₃(100) support, respectively.⁶⁷ An experimental pro argument can be found in the earlier XANES profiles scanned along the cooling cycle of similar 2% wt. Pd/γ -Al₂O₃ in CH_4^{89} instead of analogous profiles presented relative to the CH_4 contact time.⁸⁸ The absence of PdO (and of Pd⁰/PdO pair) while cooling below 960 K up to 692 K can be formally a reason for "hysteresis" drop of CH₄ conversion. $^{\rm 89}$ The authors explained the restauration of $\rm CH_4$ conversion up to 100% after following cooling below 650 K by the PdO restructuring when the NP size increases from 3.5 to 20 nm.⁸⁹ This growth of CH_4 conversion with the larger PdO size is in qualitative agreement with such results of the PdO

growing at three α -, θ -, and γ - Al₂O₃ isomorphs.¹⁵ However, the small PdO species (diameter <7 nm) were mainly amorphous ones in the last work¹⁵ while the crystal PdO structure and its transformations were controlled using EXAFS.⁸⁹ So, the question about the different electronic states on neighbor Pd atoms requires more effort to be answered within the framework of ref 15.

The crucial role of water was analyzed by tracing the presence of different components (Pd⁰, PdO_x, PdO, PdOH) of the Pd/PdO catalytic system with and without water and using ambient pressure X-ray photoelectron spectroscopy and varying temperature (473-873 K), CH₄/O₂ ratio (1:2 and 1:4).¹⁴ The authors proposed the mechanism of PdO inhibition by water (and not of the Pd surface) due to suppressed O diffusion in PdO from the bulk, which is necessary for surface PdO regeneration.¹⁴ The superposition of the morphology, particle sizes, method of the synthesis etc. often results in different conclusions about activities relative to the CH₄ oxidation at Pd deposited over different Al₂O₃ polymorphs so that the estimations for $\gamma > \alpha > \theta$ polymorphs⁹ or $\gamma > \alpha^1$ can be found in the literature. A wider picture can be obtained from the comparisons of three forms ($\alpha > \theta > \gamma$ at 12% water in the gas mixture)¹⁵ and five forms ($\theta > \delta > \kappa > \eta$ > γ for dry and wet conditions, i.e., 3% water in the gas mixture),¹³ being in agreement with $\delta > \gamma$.³⁹ The polymorphic content of Al₂O₃ oxide becomes extremely important in wet CH₄ gas mixtures because of their different hydrophobicity. The latter can be evaluated basing on the data of temperatureprogrammed desorption of water.¹⁵ The order of relative activities of the polymorphs does not vary in the dry or wet CH4 mixtures regarding the temperatures of its 50% or 90% conversions.¹³ The role of hydrophobicity turns out to be important for the zeolites when used for Pd supports.¹⁶ It is surprising that the most stable zeolite support toward to H₂O poisoning does not correspond to a maximal Si/Al modulus (tested up to 300), but to Si/Al = 40 ratio for two mesoporous USY and beta zeolites.¹⁶

The specific role of TiO₂ support was not studied in details herein. Its influence could be due to an easier O diffusion relative to that in Al₂O₃, SiO₂, etc. that creates the better conditions for surface PdO regeneration. It is confirmed by the fact that the additions of TiO₂ to any support $(Al_2O_3)^{91} SiO_2)^{92}$ ZrO_2^{93}) always allow one to produce an intermediate oxide mixture with the lower temperatures at the same conversion for CH_4 oxidation than that of pure oxides, i.e., 10% wt TiO₂ in SiO_2 , Ti/Zr = 3/2 in ZrO₂, and Ti/Al = 1/8 in Al₂O₃.⁹¹⁻⁹³ The authors explained this result by the high oxygen mobility and moderate reducibility of the resulting mixed systems.^{91,93} In the case of SiO₂, the formation of the Si–O–Ti bonds was considered as the reason for the higher activity toward CH₄.⁹² In this sense, the unusual reactivity of interfacial sites remains an important topic for future studies. Favor position of reactive sites at the interface was developed for CO dissociation⁹⁴ and hydrogenation⁹⁵ with oxygen of CO coordinated to the oxygen vacancy at the TiO₂ surface⁹⁴ and rare earth cation,⁹⁵ respectively. The Pd charge differences in the Pd/PdO pair (if it is important for CH_4 dissociation as concluded in ref 88) could be achieved for Pd pairs of the contact layer owing to the interaction with cations and anions of a support. This Pd charge difference is the reason for high Pd reactivity shown theoretically in the dissociations of $H_2O_1^{66,67}$ CH_4^{67} O_2^{67} at Al_2O_3 ,⁶⁷ and rutile-TiO₂.⁶⁶

Possible difficulties in interpreting CH₄ oxidation may be related to the mechanism's shift between different temperatures.¹⁷ The authors of ref 17 selected three experimental works^{28,96,97} for testing their kinetic modeling of CH_4 oxidation at PdO(101) in three respective temperature domains. A qualitative agreement of kinetic orders for CH₄, O_{2} , and H_2O with the experiment in the lower (570–630 K) and higher (780-870 K) temperature ranges was achieved under the condition that the reaction proceeds from the gas phase at 780-870 K. The reasonable idea of the mechanism's shift¹⁷ requires a more accurate choice of the experimental landmarks for testing because PdO(101) formation was not confirmed in refs 96 and 97. In these experimental works,^{96,97} direct oxidation of polycrystalline Pd foil was performed, which does not guaranty the synthesis of PdO(101). The barrier of 1.30 eV in the lower (570-630 K) temperature interval could be a consequence of amorphous PdO (with a reduced activity with respect to CH₄) because of analogous PdO growth at any Pd plane or Pd foil as shown in ref 24. The following transformation of amorphous PdO to crystalline ones with a better turnover-of-frequency (TOF) and the lower $E^{\#}$ can be prompted with temperature.^{25,81} Together with a 34% error of activation energy within the 570–630 K range,¹⁷ this indicates one of the remaining questions in this topic.

As we noted in part 3.4, one cannot compare the stabilities of γ -Al₂O₃(100) and γ -Al₂O₃(110) due to different stabilization of respective support models (H capping atoms in the first case) but it is possible to analyze the relative participation of different PdO facets at these oxide planes. The difference of the PdO activity (via the lowest $E^{\#}$) calculated for both PdO(100) and PdO(001) between (100) and (110) planes of γ -Al₂O₃ is minor (less than 0.1 eV in Table 6), i.e.,1.08 and 1.01 eV for PdO(100) and 0.62 and 0.56 eV for PdO(001). Analogous modeling of reaction over PdO(010) succeeded herein only for γ -Al₂O₃(100) or Al₄₈O₇₂H₁₆. It signifies that the activity of any of these two PdO planes over a γ -Al₂O₃ used for CH₄ oxidation is crudely the same at γ -Al₂O₃(100) or γ -Al₂O₃(110).

The PdO(100) plane was obtained on amorphous SiO₂/NaCl(001),³⁶ mainly as PdO(200) at γ -Al₂O₃²⁷ while PdO(001)^{34,35} and PdO(101)³⁰ were grown on Pd without other support. The PdO(101) was obtained at Al₂O₃ and possibly at amorphous SiO₂/NaCl(001) upon pure O₂ oxidation of deposited Pd but the authors did not succeed to determine respective interplane distances.³⁶ The PdO(110) plane was obtained mainly as PdO(220) at γ -Al₂O₃.²⁷ Hence, the important question for a selection between these two PdO(100) and PdO(001) forms stabilized at Al₂O₃ herein with a drastic deviation of the *E*[#] values is the extent of the Pd/PdO equilibrium with small variation of Gibbs energy (-6 kJ/mol) within the interval of traditional NP sizes (1.8–8.8 nm)⁴ is a fundamental point related with kinetic character of the redox cycle. Its shift to the side of PdO is usually achieved by varying the O₂ and CH₄ pressure.⁴

Frequent PdO(001) and PdO(101) formation without support (over Pd itself)^{34,35} and PdO(100) formation with supports,^{27,36} respectively, possibly show that the oxidation of PdO/Pd over oxide supports proceeds up to full Pd transformation to PdO. Otherwise, the reduction of a partly oxidized Pd system should also lead to PdO(001)^{34,35} or PdO(101),^{30–33} starting from remaining Pd part. Such PdO growth from external surface toward the Pd/support contact

does not correspond to a steep layer-by-layer PdO formation which can be evidently influenced by the support. But according to ref 27, namely such process takes place even starting from deposited NPs with initially dominating Pd(111)plane. The lowest layer of Pd interacts tightly with the support. As demonstrated in Table 3, its charge remains nearly the same as in respective oxide slab (if its contact PdO layer contains the Pd atoms as PdO(001)) thus facilitating the final reconstruction of oxide. If the initial fraction of $Pd(111)/\gamma$ -Al₂O₃ is too high as in ref 27, then this step of Pd⁰ conservation could be effective after the Pd(111) transformation to Pd(100) during some initial redox cycles. Then $PdO(001)^{34,35}$ or $PdO(101)^{30,32,33,36,82}$ can be formed at Pd(100) together with a smaller PdO(100) fraction which usually dominate over alumina surface. Finally, the (001) and (110) planes could easily be grown from PdO powder by vapor-transport method, but not (100).⁹⁸ The unique O type at these planes could not be a problem regarding the concept of two mechanisms of CH₄ oxidation over PdO.⁹⁹ This model was critically analyzed later also on the basis of ${}^{18}\text{O}$ isotopic analyses of CO₂ and H₂O products and a sufficiency of one surface O type was evidenced allowing different rates of the CO₂ and H₂O desorption.¹⁰⁰

This idea looks too simple, requiring complex experimental procedure (kinetic regime which hinders the formation of the most stable PdO(100) plane well adopted to γ -Al₂O₃ or other supports with tetragonal symmetries, but three arguments could be mentioned as a support of this hypothesis. First, the conclusion of Hicks et al.¹⁰¹ about higher activity of PdO over Pd crystallites than those of PdO over alumina is accompanied by the words: "Thus, the extent of palladium oxidation during reaction determines the number of catalytic sites."¹⁰¹ This phrase is exactly in line with the idea that the partial Pd oxidation will create a condition for growth of more active PdO(001), PdO(010), and PdO(101) over Pd species. But the later results about the stability of various Pd planes^{32,33,35} allow adding "activity" to this phrase to expand "the number of catalytic sites" only.

Second, in the literature,¹⁰² the success of mixed 0.1% wt Pd-0.25% wt $Co/\gamma-Al_2O_3$ catalyst was assigned to the stabilization of Pd^0 and its coexistence with PdO, which may result in a higher fraction of active PdO(001) plane in the system. Unfortunately, the XRD analysis of the Pd surface was not realized therein¹⁰² to support this argument. But from XPS data (Table 4 from ref 102), one can estimate the maximum Pd fraction of Pd⁰ (29%) and minimum Pd fraction of Pd/ Al_2O_3 (21%) as compared to other catalysts in the proposed series. This higher Pd⁰ fraction could be the source of the active PdO part without a contradiction with our proposition and in a full agreement with the conclusions of ref 101.

Third, some of us concluded in a previous paper¹⁰³ devoted to activity of Pd/La_2O3 - CeO_2 - Al_2O3 systems that the observed decrease in activity could be assigned to the increase in PdO/Pd above its optimal value at the applied conditions.

Finally, the idea of an inverse relationship between stability and higher reactivity of PdO correlates with the requirement for more undercoordinated atoms at the PdO plane.^{8,9} But our formulation proposes macroscopic parameters (like γ or ΔU_1) for the estimations of the reactivity toward CH₄. The decrease of the Pd and/or O coordination with the stability could be confirmed by comparing the Pd and O coordination numbers at the low index planes considered herein with respect to the stability which crudely obeys to (100) > (101) ~ (010) > (001) sequence (Table 7). The number of the Pd nearest

Table 7. Atomic Pd and O Coordination at the Low IndexPlanes of PdO

Туре	Pd	0	Figure
100	7(4O + 3Pd)	3	1c
101 ^{<i>a</i>}	5(3O + 2Pd)	3	1e
010	4(2O + 2Pd)	3	1d
001	8(4O + 4Pd)	2	1f

^aWhile comparing we omitted the 4Pd neighbors for Pd atom at the (101) plane because of the distances longer than 3.1 Å. In other cases, Pd–O distances span the range between 2.7 and 2.9 Å.

neighbors (NN) falls from 7 for (100) to NN = 4 for (010) (from top to bottom in Table 7). The lowest 2-coordinated O atoms occurs only at the (001) plane only where Pd is tightly bonded (NN = 8). The last plane can be joined with the support in different ways. But our attempt to "deposit" PdO(001) by Pd atoms at the top (Figure S2e) was not successful with worse stability -10.097 eV/PdO (Table S1). This PdO(001)/Al₂O₃ connection could be improved using the shifting and optimization as we developed recently.⁶⁶ But this task has not been yet realized. Irrespective of its final stability (possibly, rather high regarding other supports) it cannot change the current conclusions.

5. CONCLUSIONS

The stability of PdO(klm) planes was discussed in terms of the U_1 energy per PdO pair and surface energy γ for PdO deposited over a series of supports (monoclinic and tetragonal ZrO_2 , anatase and rutile forms of TiO_2 , γ -Al₂O₃(110), and γ - $Al_2O_3(100)$). The energy per PdO pair was calculated and showed the $|U_1(100)| > |U_1(010)| > |U_1(001)|$ order (omitting one PdO(101) model). Two exclusions for PdO(010) are obtained over γ -Al₂O₃(100) plane ($|U_1(010)| < |U_1(001)|$ for the defective $Al_{43}O_{64}H_8$ model (oxygen rich surface) and $\gamma\text{-}$ $Al_2O_3(110) (|U_1(100)| \sim |U_1(010)|)$. The opposite activity (expressed via activation barriers $E^{\#}$) of these planes relative to CH_4 dissociation was obtained in agreement with $E^{\#}(100) >$ $E^{\#}(001)$ partly known from other theoretical results obtained without oxide supports. The behavior of surface energy γ is very similar to that of U_1 . The possibility to stabilize a larger fraction of PdO(001) or PdO(010) could be a way to a higher activity of PdO. These PdO(001) or PdO(010) planes were often obtained on a Pd support while PdO(100) is usually the most stable on all oxide supports studied herein. The influence of the oxide supports could be suppressed if Pd undergoes a partial oxidation so that PdO regrows mainly on the Pd ground which remains and determines the formation of new oxide upon reoxidation. Such PdO reconstruction toward its active planes seems to start from the Pd atoms adopted to the selected support. The best recommended mechanism for all oxides except of γ -Al₂O₃(110) is thus directed by PdO \Leftrightarrow Pd cycle at the conserved Pd slab which stabilizes active PdO planes. At the γ -Al₂O₃(110) support the active PdO(010) plane is between the most stable ones. The role of the oxide supports is assigned to the Pd(111) to Pd(100) transformation during the first redox cycles as demonstrated for γ -Al₂O₃ by Garbowski et al. We remind the reader that all the oxides considered above belong to tetragonal syngony (except of monoclinic ZrO_2) when such transformation to Pd(100) is straightforward instead of Pd(111). The higher quantity of undercoordinated atoms at the PdO occurs at the less stable PdO planes so that the inverse relationship between the PdO

stability and its higher reactivity correlates with the link between the number of undercoordinated atoms and the reactivity of PdO plane or PdO/Pd interface.^{8,9}

The calculated similar charges of the Pd and PdO slabs on the same oxide support indicate the importance of Pd contacts in the first layer (Pd or PdO) and allow proposing a special role of the contact Pd layer in PdO formation. At least, the charge conservation of the contacting layer between Pd or PdO cannot lead to electrostatic barrier at the last stage of Pd oxidation in accordance with Cabrera–Mott mechanism often adopted for the oxidation.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c02946.

Extended version of Table 2 (Table S1), surface energies of initial oxide slabs (Table S2), calculated strains of PdO slabs (Table S3), Bader charges (Table S4), spatial parameters for pDOS analyses (Table S5), and additional illustrations of the reactions (Figure S1), deposited oxides (Figures S2, S3, S5, S6), supports (Figure S4), and pDOS structures (Figure S7) (PDF) Steps of CH₄ dissociation over PdO(001)/a-TiO₂ (can be seen using wxMacMolPlt⁶⁵) (XYZ) Steps of CH₄ dissociation over PdO(001)/Al₅₆O₈₀(can be seen using wxMacMolPlt⁶⁵) (XYZ)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the Bulgarian Science Fund for financial support through Contract KII-06-RUSSIA-22 and the Russian Foundation of Basic Researches within Grant 20-53-18001-Bolg_a. The research was carried out using the equipment of the shared research facilities of the Joint Supercomputer Center of the Russian Academy of Sciences and HPC computing resources at Lomonosov Moscow State University.¹⁰⁴ The authors also acknowledge the Plateforme Technologique de Calcul Intensif (P.T.C.I.; http://www.ptci.

unamur.be), located at the University of Namur, which is part of the Consortium des Equipements de Calcul Intensif (C.E.C.I., supported by the F.R.S.-FNRS, Belgium; http:// www.ceci-hpc.be).

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(107) It is possible that the same mechanisms of Pd growing occur during PdO reduction. Using different reducing media (H_2 or CH₄), the authors²⁵ noted a possible choice for PdO reduction via Pd shell formation like in the Stranski–Krastanov regime (CH₄) or through Pd islands as in the Frank–van der Merwe (H₂) regime.

(108) In order to hold the scale in the Figure 3b, two points for the amorphous PdO model (a-Pd₆₄O₆₄) are omitted due to a very high value of γ of 305.7 meV/Å².