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# Oxidation of Methane to Methanol over Single Site Palladium Oxide Species on Silica: A Mechanistic view from DFT

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## Abstract:

A theoretical analysis was carried out on the mechanism of methane oxidation to methanol occurring on single site palladium oxide species  $[\text{PdO}]^{2+}$  supported on a model of Al-MCM-41 silica. Both 6 and 8-membered ring structures were considered to represent the support. The energy profile for each elementary reaction was determined from density functional theory calculations with the OPBE functional. The calculated overall activation energies are close to the experimental values. Our calculations confirm that spin inversion can play a significant role in decreasing the barrier heights for the pathways. Indeed, in this type of reactions we could show a crossing between singlet and triplet reaction paths. We showed that the mechanism for the C-H bond cleavage and for the formation of methanol has a radical nature. According to our results, the  $[\text{PdO}]^{2+}$  species located on a 8-membered ring of silica is more active than that deposited on a 6-membered ring. The calculated activation energies to cleave the methane C-H bond are 35 and 84 kJ/mol for the radical and ionic pathways, respectively. The activation barrier and the transition state geometry of this H-abstraction step are directly correlated with the optimal angle at which the substrate should approach the  $[\text{Pd}=\text{O}]^{2+}$  moiety, with the elongation of the Pd-O<sub>oxo</sub> bond and finally with the energy of the  $\pi^*$  acceptor orbital.

## 1. Introduction

The catalytic combustion of methane has received much attention in the last decade due to its increasing application in environment-friendly fuel combustion with reduced emission of nitrogen oxides.<sup>1-4</sup> Numerous catalysts have been used, the most popular supported noble metals such as Pd, Pt and Rh<sup>5</sup>, and common transition metal oxides or mixed metal oxides as bulk or supported catalysts.<sup>6</sup> Recently, supported palladium appeared to be a highly active catalyst for the direct oxidation of methane.<sup>7-11</sup> Several studies have shown that PdO is the active phase for the catalytic combustion of methane.<sup>5,12</sup> The mixture of Pd metal and PdO was proposed to be key for the activity in Pd loaded on zeolites.<sup>13</sup> Furthermore palladium supported on acid silica-alumina amorphous mesoporous supports, such as Al-MCM-41 or SBA-15, is an excellent heterogeneous catalyst for the direct oxidation of methane.<sup>7,14</sup> Because of this, supported palladium oxides have been widely studied.<sup>3-13</sup> The oxidation state, dispersion, oxide nature and the morphology of the particles are dependent on the preparation method and on the nature of the support, which complicates the characterization efforts to elucidate the nature of the active site for methane oxidation. Experimental studies confirmed that the cleavage of the strong C-H bond in CH<sub>4</sub> is the rate-determining step for the catalytic oxidation of methane.<sup>15</sup> Quantum mechanical investigations can provide complementary information to that obtained from experimental studies and go further in the comprehension of the mechanism. They compared single-crystal surfaces of well-defined phases of palladium oxide, to clarify the mechanism on a single phase.<sup>16-19</sup> The active phase of Pd for CH<sub>4</sub> combustion has been investigated by DFT calculations and in situ SXRD experiments. It was found that the PdO(101) facet develops preferentially during the oxidation of Pd(100)<sup>17,18</sup> and that the formation of PdO(101) coincides with increased rates of methane oxidation during reaction at millibar pressures.<sup>19</sup>

In addition to these studies of PdO nanoparticles or surfaces, the gas-phase C-H bond activation of CH<sub>4</sub> by various single transition-metal-oxide ions and bare metal cations has been experimentally and theoretically investigated by a large number of groups.<sup>16-23</sup> Schwarz's group has systematically examined the efficiency and product branching ratio of the gas phase reactions of various transition metal oxide ions with methane. It was found that transition metal oxide ions ScO<sup>+</sup>, TiO<sup>+</sup>, VO<sup>+</sup> and CoO<sup>+</sup> do not react, while other transition metal oxide ions, MnO<sup>+</sup>, FeO<sup>+</sup>, NiO<sup>+</sup>, PtO<sup>+</sup> and OsO<sup>+</sup>, react with methane to give methanol. The mechanism for the methane-to-methanol conversion is suggested to occur as follows:  $MO^+ + CH_4 \rightarrow OM^+(CH_4) \rightarrow TS1 \rightarrow HO-M^+-CH_3 \rightarrow TS2 \rightarrow M^+(CH_3OH) \rightarrow M^+ + CH_3OH$ .<sup>20,21</sup>

Mebel et al.<sup>22</sup> have theoretically studied the potential energy surface (PES) for the  $\text{MO} + \text{CH}_4$  reactions (M : Sc, Ni, and Pd) using density functional calculations and suggested for NiO and PdO that the methane conversion occurs via the formation of a methyl radical. Additionally, Baerends et al.<sup>23</sup> have comprehensively studied the potential energy surfaces for methane activation by metaloxo species, showing that the lower the  $\text{MO}^{2+}$  (M = V, Cr, Mn, Fe, Co) acceptor orbital lies in energy, the lower the H-abstraction barrier is in general. Only a few theoretical studies were performed for C–H bond cleavage on zeolite supported Pd catalysts. Some researchers have investigated the C–H bond activation of methane on PdO/H-BEA<sup>24</sup> and PdO/HZSM-5.<sup>25</sup> In the latter study, the activation energy of methane dissociation depends on the local structure of dispersed PdO, while the activation energies over 6-membered rings and 7-membered rings are 98 and 94 kJ/mol, respectively. Some authors claim that intermediate pore sizes like in 10 membered ring zeolites are more beneficial to the catalytic activity than smaller or larger ones.<sup>9</sup>

Beside PdO oxide, other oxidized forms of palladium in mesoporous materials have been proposed.<sup>26-30</sup> A number of studies have been made on the  $\text{Pd}^{\text{IV}}$  oxo species. It has been proved that the calcination of  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  exchanged with Mordenite zeolite<sup>31</sup> or with acid silica–alumina amorphous mesoporous support<sup>7,32</sup> in  $\text{O}_2$  gives  $\text{Pd}^{\text{IV}}$  oxo species associated with the Brønsted acid sites. Gannouni et al.<sup>32</sup> recently reported a density functional theory (DFT) investigation of the structure of oxidized forms of Palladium in Pd/Al-MCM-41 after calcination, and compared their findings with experimental evidence obtained from IR and Raman spectroscopy and EPR observations. This catalyst (PdO/Al-LUS(9/46) has an excellent combustion activity for methane.<sup>7</sup> However, none of these studies considered the effect of the grafting sites of the Pd oxo species on the catalytic activity. To our knowledge, no theoretical study of methane activation on Al-MCM-41 supported Pd oxo single site catalyst has been previously reported.

In the present study, such a theoretical investigation is proposed to study the mechanism of the reaction of  $\text{CH}_4$  with single site  $\text{Pd}^{\text{IV}}$  oxo species supported on models of Al-exchanged MCM-41. The standard state for all species present in the gas phase was taken to be 1 atm. To study the effect of the support nature on the catalytic activity, we considered palladium oxo species supported in 6 or 8-membered rings. An important point in the catalytic process is the formation of PdO by oxidation of the deposited Pd species and then the regeneration of the oxide after the activation of  $\text{CH}_4$ . The general picture is that  $\text{O}_2$  will interact on the reduced Pd site and participate in the oxidation of methane or methanol, restoring the PdO structure.

However this point is out of the scope of the present work and will be addressed in a future study.

## 2. Computational models and methodology

### 2.1. Theoretical Models

Several patterns of acid silica-alumina were considered to model the various topological forms that can be met on an amorphous surface. The models were built using structures of silsesquioxane type that simulate the 6 ( $\text{H}_{14}\text{Al}_2\text{Si}_{10}\text{O}_{18}$ ) and 8 ( $\text{H}_{18}\text{Al}_2\text{Si}_{14}\text{O}_{24}$ ) membered rings in which two Si atoms are substituted by two Al atoms (see Figure S1). The termination of these clusters was achieved by  $\text{H-Si}\equiv$  groups instead of  $\text{H-O-Si}\equiv$  groups, to avoid additional intramolecular hydrogen bonds and unrealistic physico-chemical properties.<sup>33-36</sup>

The  $[\text{PdO}]^{2+}$  species were represented by the structures shown in Figure 1. These models were chosen based on our previous study on models of mesoporous Al-MCM-41 surface sites.<sup>32</sup> In that study, we found that the analysis of the FTIR and Raman spectra coupled with the calculated reaction energies suggest that two oxidized palladium species, namely  $[\text{PdO}]^{2+}$  in a 6- or 8-membered ring, exist.

In the present study, the isolated oxidized palladium species  $[\text{PdO}]^{2+}$  supported on silica Al-MCM-41 is modeled by acid silica-alumina aggregates ( $\text{PdO}\cdot\text{MS}$ ) designated by  $[\text{PdO}]^{2+}\cdot[\text{X-MR}]^{2-}$ , where X (6 or 8) is the ring size of TO on which the Pd oxo is deposited, each ring containing two Al atoms hence giving a correct charge balance. The aluminum atoms can occupy different positions and two isomers of position were considered here for the 6-membered ring ( $[\text{PdO}]^{2+}\cdot[\text{6-MR}]^{2-}$ ) models. It has been shown previously<sup>32</sup> that the most stable  $\text{PdO}^{2+}\cdot\text{MS}^{2-}$  complexes correspond to adsorption on 8-membered rings followed by adsorption on 6-membered rings ( $[\text{PdO}]^{2+}\cdot[\text{6-MR}]^{2-a}$ ). This is in agreement with the experimental data on Pd oxo species.<sup>31,32</sup> In the following, these complexes will be more simply denoted  $[\text{PdO}]\text{-6}_a$ ,  $[\text{PdO}]\text{-6}_b$  and  $[\text{PdO}]\text{-8}$ . Figure 1 shows the structures of the clusters and the various sites for the aluminum atoms.

On these models, we used density functional theory (DFT) to calculate the PES for the first oxidation step of  $\text{CH}_4$ :  $\text{PdO}\cdot\text{MS} + \text{CH}_4 \rightarrow \text{Pd}\cdot\text{MS} + \text{CH}_3\text{OH}$ .

### 2.2. Methods

All calculations were performed using the Gaussian 09 program<sup>37</sup> within Density Functional Theory (DFT) using the OPBE<sup>38</sup> functionals that has already proven a reasonable accuracy for the electronic structure, which concurs with available experimental observations<sup>39</sup> and

catalytic reactivity.<sup>40</sup> Moreover, some typical energies have been calculated for several experimentally available species with the OPBE, PBE and OLYP functionals and compared with the experimental values. These calculated energy data are summarized in Table S1. For example, the reaction enthalpy ( $\Delta_r H^\circ$ ) of  $\text{CH}_4 \rightarrow \text{CH}_3^\bullet + \text{H}^\bullet$ ,  $\text{H}_2\text{O}_2 \rightarrow \text{HOO}^\bullet + \text{H}^\bullet$ ,  $\text{H}_2\text{O}_2 \rightarrow 2\text{OH}^\bullet$  and  $\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}^\bullet + \text{H}^\bullet$ , are in good agreement with the corresponding experimental observations.<sup>41-43</sup> The triple- $\zeta$  plus polarization basis set (TZVP)<sup>44</sup> was used for the following atoms: silicon, oxygen, aluminum and hydrogen. For palladium, the pseudopotential of Hay and Wadt has been used together with the LANL2 basis sets as implemented in the code. The  $[\text{PdO}]^{2+}$  species bonded to silica were treated as free standing molecules.

The optimized structures were characterized by frequency calculations, and all energies include the zero-point vibrational energies unless otherwise stated. Transition-state structures (TS) on the potential energy surface were located using the synchronous transit-guided quasi-Newton method. Unrestricted DFT was used for all calculations of the singlet, triplet and quintet PES. All TS were verified by the presence of a single imaginary frequency corresponding to the reaction coordinate to ensure that the TS led to the reactants and products of interest. In addition to visualization of the imaginary vibrational mode, the intrinsic reaction coordinate (IRC) was followed in both directions. The atomic charges were calculated using the approach proposed by Mulliken.<sup>45</sup>

### 3. Results and discussion

#### 3.1 Geometric structure and electronic and bonding characteristics of the $[\text{PdO}]\text{-6}_a$ , $[\text{PdO}]\text{-6}_b$ and $[\text{PdO}]\text{-8}$ complexes.

The optimized structures of  $[\text{PdO}]\text{-6}_a$ ,  $[\text{PdO}]\text{-6}_b$  and  $[\text{PdO}]\text{-8}$  were obtained taking the total charge as neutral and considering either singlet (s) or triplet (t) or quintet (q) ground states. Except  $[\text{PdO}]\text{-6}_b$  (t and q) and  $[\text{PdO}]\text{-8}$  (q), that are  $d^6 \text{ML}_5$ , all these complexes are of  $d^6 \text{ML}_4$  type. For  $[\text{PdO}]\text{-6}_a$  and  $[\text{PdO}]\text{-8}$  the triplet state is the ground state, while the ground state of  $[\text{PdO}]\text{-6}_b$  is singlet (Table S2 in SI, Supplementary Information). The latter is the most stable of the 6-membered rings. The optimized structures are shown in Figure 1. The Pd atom interacts with four or five oxygen atoms including three (or four) Al-MCM framework oxygen atoms ( $\text{O}_{\text{MS}}$ , MS for mesoporous support) and one forming the oxo species. The framework O atoms are in any case neighbors of one Al atom. The  $\text{ML}_4$  type complexes are approximately planar, except in structures  $[\text{PdO}]\text{-6}_a$  (t and q) where the oxo oxygen atom is

positioned out of the ring. In the  $ML_5$  complexes,  $PdO^{2+}$  is located perpendicular to the ring, which makes it more accessible to methane. The most noticeable geometric feature in the singlet electronic states is a fairly long Pd–O<sub>oxo</sub> bond in comparison with that in the species with the triplet and quintet states (194 pm in singlet vs. 178 pm in quintet and 186 pm in triplet (Figure 1)). The distances between the palladium ion and the framework oxygen atoms vary between 206 and 259 pm (Table S1).

The different acidity of the oxygen atoms ( $-Al-O_{MS}$ ) interacting with  $Pd^{4+}$  is reflected by the computed Mulliken charges, the ligand framework oxygen atoms ( $O_{MS}$ ) donating electron to the palladium center, which decreases the positive charge on the metal (Table S3 in SI). In singlet spin states, the palladium atom is the least positively charged and the oxo oxygen is the most negatively charged.

### 3.2. Reaction profiles.

The structures of the model clusters used in this work are shown on Figure 1 and the Pd–O distances are given in Table S2 (SI). They are either of  $ML_4$  or  $ML_5$  type depending on the size of the ring and on the spin state.<sup>32</sup> The approach of methane to these clusters leads to loose precursor states (PS) (Figure S2). In the final state (FS), methanol is bound to the palladium atom, either by oxygen as a ligand or by hydrogen forming a loose complex, depending on the coordination of the metal (Figure S3).

Two possible reaction pathways for the C–H bond activation of methane, and the further conversion to methanol can exist, a radical mechanism and an ionic mechanism, that will be compared in the following (Scheme1).

#### 3.2.1 Radical mechanism

The radical pathway can be partitioned into two steps. First, the H atom abstraction to form the methyl radical leads to the intermediate labeled  $I_1$ , via the transition state  $TS_{1R}$  (Scheme 1). The second step is the methyl migration via  $TS_{2R}$  to form the methanol product. In some cases, a reorientation of the  $CH_3$  group leading to the intermediate  $I_2$  is necessary to ensure the formation of the C–O bond. The energy profiles for the radical pathway at the various spin states are given in Figure 2 and the activation energies of the different steps are gathered in Table 1. The geometry of the intermediates is given in Figures S3–S4 and that of the TSs in Figure 3. The main distances and angles are collected in Tables S4–S6.

### 3.2.1.a The C-H bond activation step

A first observation can be made from Figure 2. In the case of the singlet spin state, whatever the cluster, intermediate  $I_1$  does not exist and the final state is obtained directly from  $TS_{IR}$  with activation energies of 87, 107, and 89 kJ/mol for the [PdO]-6<sub>a</sub>(s), [PdO]-6<sub>b</sub>(s), and [PdO]-8(s) clusters, respectively (Table1). For the triplet and quintet states, the reaction proceeds really in two steps. In the case of [PdO]-6<sub>a</sub> the 3 transition states have a markedly different energy, and the pathway on the (ground state) triplet surface is clearly favored. For [PdO]-6<sub>b</sub> the TS on the singlet and triplet surfaces have very similar energy and reaction can occur either on the ground state singlet or after crossing to the triplet surface. For the [PdO]-8 cluster, the TS on the triplet surface is slightly favored.

The C-H bond is highly stretched for the triplet and quintet TS (140-146 pm), particularly for  $TS_{IR}$ -8(t) (149 pm) but less for the singlet TS (129 -135 pm) (Figure 3). For comparison, this stretch is smaller with other metal oxides MO (M: Ni (141pm), Pd (139 pm))<sup>22</sup> and Fe=O (126 pm).<sup>46</sup> In a parallel way, the distance between  $O_{oxo}$  and H is longer for the singlet TS (114 pm) than for the other spin states (109-111 pm). This would mean that the TS's are earlier in the singlet states than in the triplet or quintet states.

In the case of [PdO]-6<sub>a</sub> and [PdO]-8, there is a triplet to singlet intersystem crossing after the C-H bond cleavage TS since the final product (methanol) is always singlet. The reaction proceeds first on the triplet PES before reaching the  $TS_{IR}$  structure where the system can switch its multiplicity and continue on the singlet PES. Such a mechanism is termed two-state reactivity (TSR) by Shaik et al.<sup>47</sup> The spin crossing is possible because of the small difference in the energy of the two lowest spin states (22 and 11 kJ/mol for the [PdO]-6<sub>a</sub> and [PdO]-8, respectively). In the case of [PdO]-6<sub>b</sub>, the reaction can proceed via the singlet pathway directly.

The optimized structures for  $I_1$ -6<sub>a</sub>,  $I_1$ -6<sub>b</sub> and  $I_1$ -8 clusters are shown in Figure S4 (SI). Compared with the initial clusters after adsorption of the methane (PS, Figure S2), the local structure of the PdO moiety and the coordination environment of Pd change (Tables S4-S6). The distance that obviously changes the most is Pd- $O_{oxo}$  between Pd and oxygen in PdO itself and particularly in the  $I_1$ -6<sub>b</sub>(t) cluster (lengthening of 17 pm). The hydrogen atom has been completely transferred to  $O_{oxo}$ , with a O-H distance between 97 and 100 pm. This suggests that the oxygen in PdO is involved in the methane activation directly.

### 3.2.1.b Formation of methanol



In what concerns the second step, we can notice that the methyl radical in  $I_1$  is, in some cases, not well oriented to interact with OH and must rotate to yield intermediate  $I_2$  (Figure S5). In this intermediate, the  $\text{CH}_3$  moiety is oriented in opposite to the O-H bond. According to previous works, the reorientation of the methyl radical to give  $I_2$  facilitates the formation of methanol.<sup>48,49</sup> This is the case for  $I_2\text{-6}_a(\text{q})$  this rotation is quasi energy-neutral and  $I_2\text{-6}_b(\text{q})$  is less stable than  $I_1$  by 6 kJ/mol, which could be considered as a lower limit for the rotation barrier, in agreement with the barriers calculated by Shaik et al.<sup>50</sup> for the hydroxylation of methane with the enzyme cytochrome P450. In the case of  $I_2\text{-8}(\text{t})$  and  $I_2\text{-8}(\text{q})$ , these intermediates are more stable than the corresponding  $I_1$  intermediates by -7 kJ/mol and -3 kJ/mol, respectively.

It is obvious on Figure 2 that the transition state  $\text{TS}_{2\text{R}}(\text{q})$  of the second step for the quintet state is far too high, which eliminates this spin state as a plausible pathway. In opposite for the triplet state, the second step is almost barrier-less, with activation energies of 1 to 7 kJ/mol (Table 1). It results that the rate-determining step for the triplet state is the first one that is responsible for the C-H bond dissociation and the competition is between the singlet and the triplet states.

In  $\text{TS}_{2\text{R}}$ , the C-O bond formed is longer for the triplet state than for the quintet state, particularly for  $\text{TS}_{2\text{R}}\text{-8}$  (221-265 pm vs. 168-178 pm). At the same time, the Pd-O bond being broken is smaller for the triplet state, particularly for  $\text{TS}_{2\text{R}}\text{-8}$  (188-195 vs. 206-214 pm). This would mean that  $\text{TS}_2$  is later for the quintet state, in line with a higher barrier.

The desorption of methanol is endothermic on  $[\text{PdO}]\text{-XMR}$  (by 14-65 kJ/mol (s), 12-50 kJ/mol (t), 20-85 kJ/mol (q)), except for the singlet state pathway on  $[\text{PdO}]\text{-6}_b(\text{s})$  where the desorption is exothermic (Figure 2).

### 3.2.1.c The factors that influence the C-H bond activation step

For the radical mechanism, the activation energy for C-H dissociation depends on various parameters: (a) the optimal angle at which the substrate should approach the  $[\text{M}=\text{O}]^{2+}$  moiety<sup>49,22</sup>, (b) the energy of the  $\sigma^*$  or  $\pi^*$  acceptor orbital of the initial  $\text{M}=\text{O}$  complex<sup>46,40</sup>, which leads to the  $\alpha\text{-}\sigma^*$  or  $\beta\text{-}\pi^*$  reaction channel, and (c) the lengthening of the  $\text{M}-\text{O}_{\text{oxo}}$  bond in reactants.<sup>51</sup> In our system  $[\text{PdO}]\text{-MS}$ , the lowest unoccupied orbital is the  $\pi^*$  molecular orbital for all spin states and ring size. It mainly consists in the antibonding combination of  $\text{Pd}\text{-}d_{\text{xz/yz}}$  and the  $\text{O}_{\text{oxo}}\text{-}p_{\text{x/y}}$  fragment orbitals as shown on Figure S6. In the case of the singlet state, this orbital mixes with some orbitals of the frame oxygen atoms. Hence, the reaction follows the  $\beta\text{-}\pi^*$  channel. This is reflected by the fact that no  $\text{TS}_{1\text{R}}$  is linear, which would

mean a  $\alpha\text{-}\sigma^*$  channel, and the Pd-O<sub>oxo</sub>-H angle varies from 110 to 119° depending on the complex, which characterizes the  $\beta\text{-}\pi^*$  reaction pathway.

The relative energies of the  $\pi^*$  orbital of the various starting clusters are given in Table S7. Whatever the ring size, this orbital is higher in the singlet state than in the others. Based on this criterion only, the barriers should be the highest for the singlet states, which is true particularly in the case of 6<sub>b</sub>. However, we can see on Figure 1 that the Pd-O<sub>oxo</sub> bond is longer for the singlet states (194 vs. 178-186 pm), which would give smaller barriers. The two effects balance, which reduces the difference between the barriers. The same observation is done when triplet and quintet states are compared: the  $\pi^*$  orbital is higher for the quintet states but their Pd-O bond is longer. Concerning the Pd-O<sub>oxo</sub>-H angle, it is comprised between 110 and 119° in all TS<sub>IR</sub> transition states, which characterizes the  $\beta\text{-}\pi^*$  reaction pathway.

The different acidity of the oxygen atoms (-Al-O<sub>MS</sub>) affects the charge of the Pd-O<sub>oxo</sub> moiety and hence, the position of the electron acceptor orbital. For instance, the  $\pi^*$  orbital in [PdO]-6<sub>b</sub>(s) is higher in energy than in [PdO]-6<sub>a</sub>(s) (larger positive charge) and lower in [PdO]-6<sub>b</sub>(t) than in [PdO]-6<sub>a</sub>(t) (smaller positive charge). This conclusion is in agreement with previous experimental data concerning the catalytic activity of PdO that can be affected by the acidity of acid silica-alumina amorphous mesoporous support.<sup>7,14</sup>

### 3.2.2 Ionic mechanism

In the ionic pathway, the insertion of the C-H bond of methane into the Pd<sup>IV</sup>-O<sub>oxo</sub> bond occurs via a kind of metathesis mechanism. One of the hydrogen atoms in the coordinated methane shifts to the O<sub>oxo</sub> atom and the C atom binds to Pd in a concerted manner via a four-centered transition state TS<sub>1I</sub>, giving the hydroxyl intermediate, [CH<sub>3</sub>-Pd-OH]<sup>2+</sup>•MS<sup>2-</sup> (designated by I<sub>3</sub>). The second step from I<sub>3</sub> to FS via TS<sub>2I</sub> is a reductive elimination by recombination of CH<sub>3</sub> and OH to give methanol (Scheme 1). This ionic reaction pathway for the methane-methanol conversion includes one intermediate and two TS as well as reactant and product complexes. Despite several attempts, the transition states could not be located in the case of the quintet states. Hence only the singlet and triplet ionic pathways will be described in the following.

For the ionic mechanism, the first step leading to intermediate I<sub>3</sub> is exothermic due to its high stability, the reaction energy being -149 (s), -135 (t), -221 (s), -159 (t), -208 (s), -221 (t) kJ/mol for [PdO]-6<sub>a</sub>, [PdO]-6<sub>b</sub>, and [PdO]-8, respectively (Figure 4). The structures of I<sub>3</sub> are shown on Figure S7. Whatever the cluster and its spin state, the bond lengths and angles are

very similar (Tables S7-S10). A short hydrogen bond (147 to 192 pm) is formed between the H atom of [CH<sub>3</sub>-Pd-OH] and an oxygen atom of the ring (Figure S7).

There is also a spin crossing between the singlet and the triplet states during the first step. Except in the case of [PdO]-6<sub>a</sub>, where the energy barrier is slightly larger for the singlet state (134 vs. 127 kJ/mol), the barrier is far smaller for the triplet state, 84 and 135 vs. 223 and 199 kJ/mol for [PdO]-6<sub>b</sub>, and [PdO]-8, respectively (Figure 4).

The structures of the first TS (TS<sub>1I</sub>) are given on Figure 5 and the corresponding geometrical data in Tables S8-S10. For the 6-membered rings in the singlet state, the Pd-O<sub>Oxo</sub> bond decreases first in TS<sub>1I-6a</sub>(s) and TS<sub>1I-6b</sub>(s) compared to the starting point and increases again in the corresponding I<sub>3</sub> clusters. In opposite for the 8-membered ring in the singlet state, Pd-O begins to increase in the TS and to decrease afterward. For the triplet states, whatever the size, this bond increases regularly. The Pd-C bond that decreases regularly is much longer in TS<sub>1I-8</sub>(t) than in all the others, which means that this TS is early along this coordinate. However, the long C-H bond (160 pm) and the short O-H bond (106 pm) would indicate a late TS for the breaking of the C-H bond. For the 6-membered rings, the longer Pd-C and O-H bonds and the shorter C-H bond in the singlet state than in the triplet state seem to indicate an earlier TS in the former state.

In the next step, a 1,2-migration of the methyl group from Pd to O occurs to form a C-O bond (reductive elimination), also in a concerted manner via a three-centered transition state TS<sub>2I</sub> (Figure 5 and Tables S8-S10). The barriers are relatively small and the singlet pathway is easier than the triplet one, with activation energies of 37 - 47 compared to 73 - 77 kJ/mol. IRC calculations have confirmed the connection between I<sub>3</sub> and FS through transition state TS<sub>2I</sub>. In the transition state, the Pd-C and Pd-O<sub>Oxo</sub> bonds are stretched as compared to those in TS<sub>1I</sub> and a new C-O<sub>Oxo</sub> bond starts to form. The structures of TS<sub>2I</sub> in the singlet and triplet states are similar, although TS<sub>2I</sub>(t) has slightly shorter C-O<sub>Oxo</sub> bond lengths. The C-Pd-O<sub>Oxo</sub> angle in all the TS<sub>2I</sub>(s) are close to the TS<sub>2I</sub>(t) (~58°).

### **3.3 Mechanistic Features: Comparison between radical and ionic pathways and influence of support**

If the two mechanisms are compared, the energy barriers calculated for the ionic mechanism are much larger than those calculated for the radical mechanism, for the first step as well as for the second one. Hence, a first conclusion is that the activation of methane to give methanol with the studied catalyst follows a radical mechanism.

Let us consider now the size of the support ring. For [PdO]-6<sub>a</sub>, the reaction starts in the triplet state with a barrier of 82 kJ/mol and after a spin-crossing toward the single PES the singlet final product is obtained. The situation is the same for [PdO]-8 with a barrier of 90 kJ/mol. In these two cases, there is a cost for the promotion of the triplet state to the singlet state for the reactants. Minimum energy seam of crossings has not been calculated. Nevertheless, the structures of TS and intermediate states around the spin crossing are very similar. Hence geometry rearrangement at the crossing point will be minimal. The energy of the crossing is a value estimated from the difference between the energies of the singlet and the triplet namely 26 and 8 kJ/mol, respectively that must be added to the barrier.<sup>40</sup> Finally for [PdO]-6<sub>b</sub>, the reaction follows the singlet PES with a barrier of 107 kJ/mol. Hence, the global barriers are very similar (108, 107, and 98 kJ/mol for [PdO]-6<sub>a</sub>, [PdO]-6<sub>b</sub>, [PdO]-8, respectively) with a small preference for the largest system. These values are in agreement with those observed experimentally for a series of PdO/MCM-41 catalysts (80-105 kJ/mol).<sup>51</sup> In the literature also the apparent activation energy is found to range from 70 to 90 kJ/mol.<sup>52</sup> In our prior work<sup>7,32</sup> it has been shown that in PdO/Al-LUS(9/46) materials two species are likely to exist, isolated Pd atoms namely [PdO]<sup>2+</sup> in 8-membered rings and PdO particles. The activation energy ( $E_a$ ) determined experimentally for this catalyst is 90 kJ/mol (Figure S7). The values of the activation energy observed on PdO/Al-LUS(9/46) agreed with the global barriers calculated with isolated Pd atoms. To reach this conclusion, we assume that the activation of CH<sub>4</sub> is the rate determining step and do not consider the oxidation of the catalyst, as did other authors.<sup>18</sup> Moreover, it was found that the activation energy on PdO surfaces is much higher on the very stable PdO(100) termination than on PdO(101): on PdO(101) activation energies of 62 kJ/mol were calculated,<sup>18</sup> while on PdO(100) activation energies of 131 kJ/mol<sup>18</sup> and 104,2 kJ/mol<sup>17</sup> were obtained. The calculated results of the activation energy relative to isolated Pd atoms (108, 107, and 98 kJ/mol for [PdO]-6<sub>a</sub>, [PdO]-6<sub>b</sub>, [PdO]-8, respectively) seem to be reasonable compared with experimental values 90 kJ/mol, which are different for extended PdO phases. We conclude that for the PdO/Al-LUS(9/46) catalyst the CH<sub>4</sub> activation could be primarily due to isolated Pd atoms and PdO(100) phases. The reactivity of isolated Pd<sup>IV</sup> oxo sites depend on their local geometrical environment. Moreover, the  $E_a$  values for Pd/Y are much higher than those reported for Pd/ZSM-5 and Pd/mordenite.<sup>53,54</sup>

## 4. Conclusion

In this paper, we studied, with density functional theory methods, the methane C–H bond cleavage reactions catalyzed by an oxo Pd<sup>IV</sup>=O species supported on silica Al-MCM-41. We studied the effect of the support on the catalytic activity. For this purpose, we considered isolated palladium oxo species supported on 6 or 8-membered rings and calculated the PES for the PdO•MS + CH<sub>4</sub> → Pd•MS + CH<sub>3</sub>OH reaction. The concerted reaction pathway for the direct methane-methanol conversion by PdO<sup>2+</sup> can proceed via a radical or an ionic mechanism. We showed that the activation of methane to give methanol with the studied catalyst preferentially follows a radical mechanism. For the singlet states, the reaction proceeds in one step, the breaking of the C-H bond leading directly to a coordinated methanol molecule. For the triplet states on the opposite, the reaction proceeds in two steps, with rebound of the methyl radical. The Pd<sup>2+</sup> oxo species supported on a 8-membered ring is slightly more reactive than those supported on a 6-membered ring. In some cases, the reaction follows a singlet state mechanism. In others, it follows a so-called two-state reactivity (TSR) mechanism, via a spin crossing, starting from the triplet state and ending in the singlet state.

**Supporting Information available:** Calculated structures and structural parameters of various species on [PdO]-6a; [PdO]-6b and [PdO]-8 clusters; Acceptor orbital  $\pi^*$  and Arrhenius plot

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### TOC Graphic

