

Methane dissociation over Pd nanocluster: DFT study

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Abstract. Palladium is often used as a catalyst for many processes in emissions control technologies [1, 2]. This is due to its potential of becoming a novel catalyst for low temperature methane combustion [3]. Palladium nanoclusters have a number of surface features and various adsorption sites, their relative activity play important role if predictions are to be made for improved materials properties. The dissociation of methane over palladium nanoclusters and high index surfaces was investigated using density functional theory (DFT) as implemented in grid based projector augmented wave (GPAW) code [4]. Methane has been adsorbed on the Pd₁₃ nanoclusters at various active sites, and the results shows that CH₄ dissociate into CH₃ and H. It is found that CH₃ bind strongly to the top site forming a Pd-C bond of 2.050 Å and H on bridge with a Pd-H bond of 1.716 Å. Methane dissociation was found to be more favorable on the nanocluster than on Pd surfaces.

1. Introduction

Precious metal catalysts, which include the platinum group metals (PGMs) for example Pt, Pd, Rh and noble metals such as Ag and Au, find their way into processes of emissions control technology for application in methane oxidation and catalytic converters [5, 6]. The mostly used catalyst is Pt and Pt-based. Recently, Pd-based catalysts are being developed since they have similar electronic configurations and lattice constants as Pt but cheaper [7].

In recent years, metal nanoparticles have been of interest in several areas including physics and material sciences. The properties of these nanoparticles were found to differ from those of bulk materials [8-10]. In addition, nanoparticles have large surface area and are rich in defect such as steps and kinks. This enhances the activity of most reactions in the emission control technology [11].

Methane dissociative adsorption is generally assumed as the rate determining step for methane oxidation [12]. In the current study, we use the DFT calculations to understand the methane dissociation reaction process over Pd₁₃ nanocluster and compare its catalytic activity to Pd surface. This was achieved by carrying out adsorption calculations of molecules and intermediates that form part of the methane dissociation reaction on possible adsorption sites of Pd₁₃ nanocluster and Pd(100) surface. The uniqueness of the Pd nanocluster and surface under consideration is their similarity of active adsorption sites and allow comparison to be made precisely; that is the top, bridge and 4fold hollow adsorption sites.

2. Methodology

Calculations were performed using DFT as implemented in the GPAW code [4]. GPAW is an implementation of the projector augmented wave (PAW) method [13] that uses real space grids to represent the wave functions, densities and potentials. The revised version of the Perdew–Burke–Ernzerhof (RPBE) exchange correlation function was used with a grid-spacing of 0.18 Å and k-points mesh of 4x4x4 for the bulk Pd. The Pd₁₃ nanocluster was set to have a cell volume of 18x18x18. A five layered Pd(100) slab surface with a vacuum thickness of 10 Å was used in the calculations. The surface was set to be periodic along the x- and y-directions, whereas non-periodic along the z-direction. A k-mesh of 4x4x1 was used for the surface relaxation and molecule adsorption calculations.

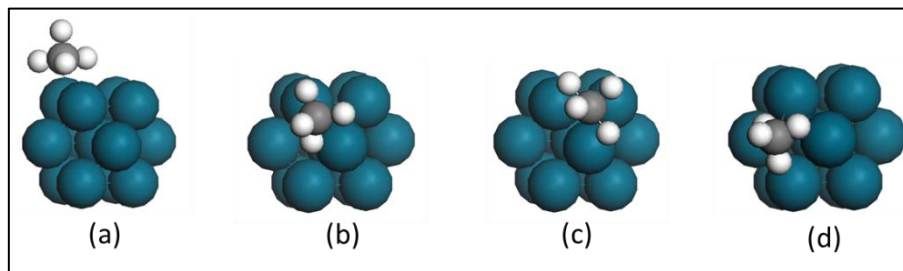


Figure 1. Pd₁₃ nanoclusters showing adsorption of CH₄ at various sites namely (a) top, (b) bridge, (c) 3fold hollow and (d) 4fold hollow.

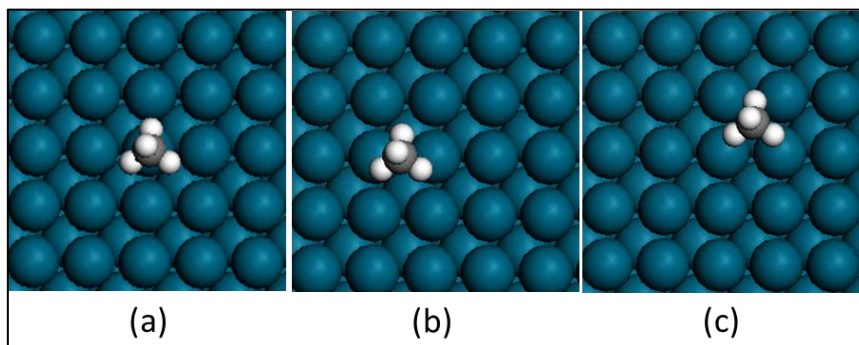


Figure 2. Top view of Pd(100) surfaces showing adsorption of CH₄ at various sites namely (a) top, (b) bridge, (c) 4fold hollow.

Pd₁₃ nanocluster consists of four adsorption sites whereas Pd(100) surface exhibits three high symmetry adsorption sites as shown in Figure 1 and 2. Different adsorbates can possibly be adsorbed on these sites and the site with the lowest adsorption energy is considered as the most preferred adsorption site. The adsorption energies for the adsorbates are calculated using the equation,

$$E_{\text{ads}} = E_{a/m} - E_a - E_m \quad (1)$$

where a represents the adsorbate and m the Pd₁₃ nanocluster or Pd(100) surface.

3. Results and Discussion

3.1. Validation of the method

The bulk Pd structure with a space group of Fm-3m was used to cleave the Pd(100) surface and create the Pd₁₃ nanocluster. The Pd nanocluster has a radius of 5 Å and consists of 13 atoms with Pd-Pd average bond length of 2.751 Å Pd(100) was set to have a 2x2 supercell with five atomic layers, where the bottom two layers were constrained while allowing the remaining three layers to relax.

The DFT method used to perform the calculations was tested and validated by determining the lattice parameter for bulk Pd structure, bond length for CH₄ molecule, Pd(100) surface and Pd₁₃ nanocluster. Note that, before the properties could be calculated, all the structures were subjected to full geometry optimization allowing cell and volume to change, and the equilibrium parameters were recorded when the structures reached their ground state energy and converged to 1 meV. We found that the lattice parameter and bond length are in reasonable agreement to the experimental results with bulk Pd value of $a = 3.983$ Å as compared to 3.891 Å and the C-H bond length of 1.097 Å for CH₄, as shown in table 1. Lattice parameters and bond length of bulk Pd and Pd(100) surface agrees to within 3% with the available experimental data. The Pd-Pd and C-H average bond length for Pd₁₃ and CH₄ are also in good agreement to within 1% of the experimental results.

Table 1. Lattice parameters of bulk Pd, the average bond length (C-H) for CH₄ molecule, (Pd-Pd) for Pd(100) surface and Pd₁₃ nanocluster.

| Structure | Lattice parameters (Å) | | Average bond length (Å) | |
|------------------|------------------------|--------------------|-------------------------|--------------------|
| | DFT | Experimental | DFT | Experimental |
| Pd | 3.983 | 3.891 ^a | 2.816 | 2.751 ^a |
| Pd(100) | 2.821 | 2.744 ^b | 2.850 | - |
| Pd ₁₃ | - | - | 2.751 | 2.726 ^c |
| CH ₄ | - | - | 1.097 | 1.087 ^d |

^aThe experimental lattice parameter for bulk Pd were taken from ref [14]

^bThe experimental lattice parameter were for Pd(100) were obtained from ref [15]

^cThe Pd₁₃ experimental bond length was taken from ref [16]

^dThe CH₄ experimental bond length was obtained from ref [17]

3.2. Dissociation of methane over Pd₁₃ nanocluster and various Pd surfaces

Methane dissociation is determined by examining the adsorption of various molecules and intermediates that form part of the dissociation reaction. In this work CH₄, CH₃, CH₂, CH, C and H are adsorbed on various sites of Pd₁₃ nanocluster and Pd(100) surface. The preferred adsorption sites and energies of these adsorbates are listed in Table 2 We note that CH₃ prefers to be adsorbed on the top site for both Pd₁₃ nanocluster and Pd(100) surface, with a Pd-C bond length of 2.050 Å and 2.059 Å, respectively. CH₂ prefers the bridge site whereas CH and C prefer various hollow sites depending on the adsorbents. The H prefers bridge adsorption site on the nanoclusters with Pd-H bond 1.716 Å, whereas on the Pd surface, H will likely be adsorbed on the 4fold hollow adsorption site. Interestingly, adsorption of CH₄ on Pd₁₃ nanocluster gives -0.51 eV, suggesting that the nanocluster slightly binds on the 4fold hollow site. The adsorption energy of -0.01 eV has been reported for Pd(100) by Trincherro *et al.* [11], which is less as compared to the calculated value obtained for Pd₁₃ nanocluster. However, this has been recorded for different adsorption sites.

Table 2. Preferred adsorption sites and adsorption energy (E_{ads}) of various molecules and intermediates that form part of the methane dissociation reaction (listed under adsorbate) over Pd₁₃ nanocluster and Pd(100) surface.

| Adsorbate | Pd ₁₃ | | Pd(100) | |
|-----------------|------------------|-----------------------|--------------|-----------------------|
| | site | E_{ads} (eV) | site | E_{ads} (eV) |
| CH ₄ | 4fold hollow | -0.51 | - | - |
| CH ₃ | top | 0.41 | top | 1.01 |
| CH ₂ | bridge | 1.04 | bridge | 1.64 |
| CH | 4fold hollow | 0.69 | 4fold hollow | 1.55 |
| C | 4fold hollow | 0.47 | 4fold hollow | 1.85 |
| H | bridge | -0.59 | 4fold hollow | -0.32 |

The superimposed reaction profile for methane dissociation on Pd₁₃ nanocluster and Pd(100) surface are shown in Figure 3. The dissociation of methane is denoted as a process of continuously removing hydrogen from CH₄ during the interaction of methane with the Pd nanoclusters and surfaces. The dissociation of methane is then expressed by equation (2) – (5):

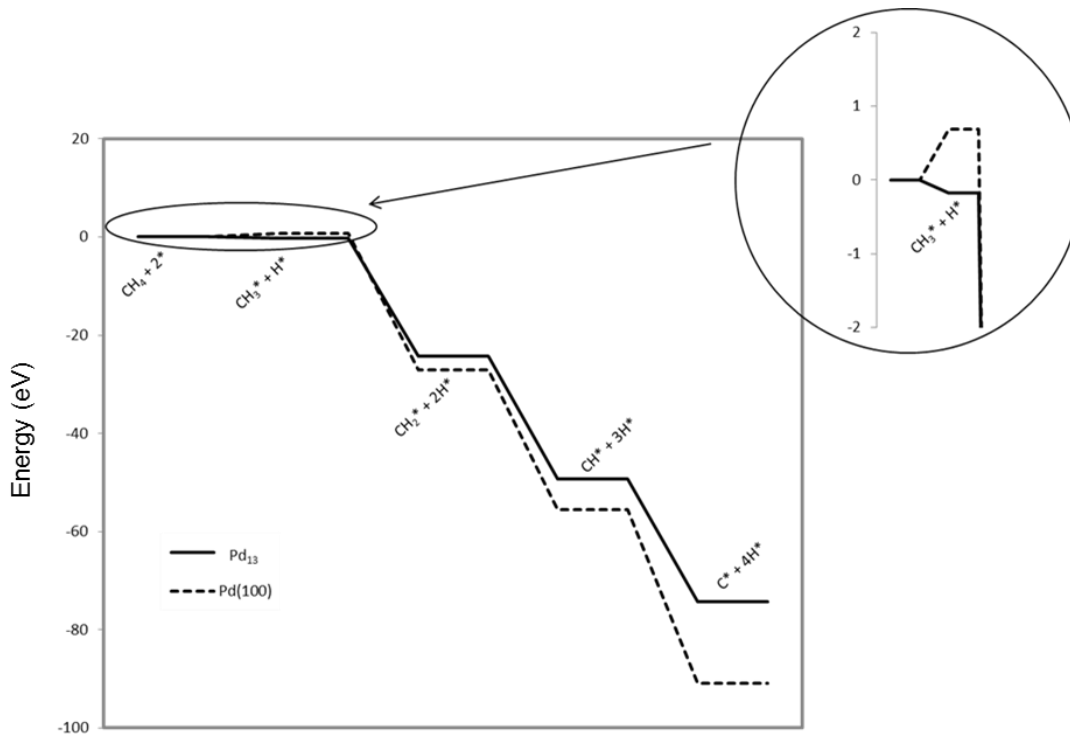


Figure 3. The superimposed reaction profile for methane dissociation on Pd₁₃ nanocluster and Pd(100) surface.

The reaction starts with methane in a gas phase and two identical Pd nanoclusters or Pd surfaces denoted by an asterisk (*) and ends with C* and 4H*. Four possible dissociation processes are indicated. The first dissociation stage, is the production of CH₃* and H*. This process is exothermic on Pd₁₃ nanocluster whereas endothermic on Pd(100) surface. This suggests that Pd₁₃ is the most preferred adsorbent for methane dissociation at standard conditions.

Now, considering methane dissociation for the other three stages, that is, the production of CH₂* + 2H*, CH* + 3H* and C* + 4H*. The processes are exothermic on both the adsorbents. The production of C* + 4H* dominate the reaction process, showing the lowest energy. We also note that methane dissociation process is spontaneous for the Pd₁₃ nanocluster, whereas non-spontaneous for Pd(100) surface. This suggest that Pd₁₃ is more favourable as compared to Pd(100) surface.

4. Conclusion

DFT results predicted good agreement of the lattice parameters and bond lengths with experiments to within 3% and 1%, respectively. Furthermore, adsorption of various adsorbates on three and four possible adsorption sites reflect lower adsorption energies for Pd surface and nanocluster, respectively. It was obtained that CH₃ prefers the top site on Pd₁₃ nanocluster whereas CH₂ and H prefer the bridge. Furthermore, both CH and C prefers 4fold hollow adsorption site. The first dissociation stage of methane, is observed when CH₄ dissociates into CH₃* forming a Pd-C bond of 2.050 Å and H* with a Pd-H bond of 1.716 Å on Pd₁₃ nanocluster. Methane dissociation over Pd₁₃ nanocluster is favorable for all the dissociation stages under standard condition, and thus considered the most preferred adsorbent as compared to Pd(100) surface.

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