

# Density functional theory study of methane activation over PdO/HZSM-5

Jian-guo Wang<sup>1</sup>, Chang-jun Liu\*

Key Laboratory for Green Chemical Technology and School of Chemical Engineering,  
Tianjin University, Tianjin 300072, PR China

Received 5 June 2005; received in revised form 22 November 2005; accepted 28 November 2005  
Available online 6 January 2006

## Abstract

Methane is one of the most stable molecules. The first C–H bond activation of methane is a crucial step in methane conversion. Once the first C–H bond was broken, the remaining C–H bonds could be very easily activated. In this work, DFT study of the first C–H bond activation of methane over PdO/HZSM-5 catalyst for methane combustion was conducted. The 7T(6, 1) and 6T cluster models, correspond to the  $\alpha$ - and  $\beta$ -sites of ZSM-5 that take 85–100% of the total metal sites in the zeolite, were chosen for the study. The physisorbed state of methane and the transition state geometries of the first C–H bond dissociation were obtained. The study confirms that the oxygen in PdO directly involves in methane activation that means PdO is the active Pd species. The proton in the zeolite promotes the methane activation via the formation of H<sub>2</sub>O with OH, formed during methane activation over PdO. The barrier energy was also calculated. The activation energy of methane dissociation over 6T1Al and 7T1Al-PdO/HZSM-5 is 98 and 94 kJ/mol, respectively, while the activation energy over 6T2Al and 7T2Al-PdO/HZSM-5 decreases 16 and 22 kJ/mol, compared to that over 6T1Al and 7T1Al clusters. This suggests more acidic sites would reduce the activation energy for methane activation.  
© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Density functional theory; Methane combustion; Methane activation; PdO/HZSM-5

## 1. Introduction

Catalytic combustion of methane can significantly reduce emission of nitrogen oxides, and consequently has drawn a lot of worldwide attention [1–7]. Palladium-based catalysts have been proven to be as the most effective for the complete oxidation of methane to carbon dioxide and water [2–7]. Previous studies have confirmed that PdO is the active species for the catalytic combustion of methane [5–7]. These studies suggested that the reaction follows Mars and van-Krevelen mechanism [8,9], a redox one, which involves the activation of a C–H bond in methane by Pd<sup>2+</sup>O<sup>2-</sup> ion pairs through a heterolytic mode [5,10]. The rate-determining step is the breaking of the first C–H bond in methane for the catalytic combustion of methane [10–12]. Once the first bond is broken, sequen-

tial reactions to form CO<sub>2</sub> and H<sub>2</sub>O are much easier [10]. Therefore, an investigation of the activation of the first C–H bond in methane molecule is important to better understand the catalytic mechanism and thereby further to improve the catalyst.

Previous investigations have demonstrated that the support (zeolite) can affect the dispersion and oxidation of the supported Pd and thus affect the catalytic activity and stability [2,6,11]. Okumura et al. confirmed that the activity and durability of Pd is considerably dependent on the kind and the amount of acid in the zeolite [6]. To further understand the reaction mechanism, several investigations have been conducted to determine the local structure of PdO/HZSM-5 and the relationship between dispersed PdO and the acid sites of HZSM-5 [13–17]. Bell et al. proposed the principal active species to be Z<sup>-</sup>H<sup>+</sup>(PdO) or Z<sup>-</sup>H<sup>+</sup>(PdO)H<sup>+</sup>Z<sup>-</sup>, where Z<sup>-</sup> represents the aluminium site in the zeolite [16,17]. Okumura et al. used EXAFS to show that the local structure of dispersed PdO is similar to that of the bulk PdO, a four-coordinated square planar structure [13–15]. We have previously performed a density functional theory (DFT) study of the structural and electronic properties of PdO/HZSM-

\* Corresponding author. Tel.: +86 22 27406490; fax: +86 22 27890078.  
E-mail address: [ughg\\_cjl@yahoo.com](mailto:ughg_cjl@yahoo.com) (C.-j. Liu).

<sup>1</sup> Present address: Department of Physics and Astronomy, University of Aarhus, Dk-8000 Aarhus C, Denmark.

5 [18] and the results obtained in that study were consistent with the experimental results [13–17].

Relatively few theoretical investigations of methane dissociation over PdO catalyst have been conducted. A theoretical understanding of methane dissociation is a very important fundamental issue. Previous investigations have focused on methane dissociation over a transition metal by using first-principle DFT methods [19–22]. Broclawik et al. studied the electronic structure of bare PdO and Pd<sub>2</sub> and the interaction between these species (PdO and Pd<sub>2</sub>) and a methane molecule by means of DFT [23,24]. Tonetto et al. applied the Extended Hückel Molecular Orbital approach to study methane oxidation on Pd catalysts [25]. In that study, the Pd catalyst was modeled by different Pd or PdO surfaces. In order to investigate the effect of chlorine on the catalytic activity, a PdO model containing chlorine was also studied [25]. Hwang and Mebel investigated the potential energy surface for the reactions of PdO with methane by using DFT calculations [26]. However, none of these studies considered the effect of the support on the catalytic activity. To our knowledge, even no theoretical study of methane activation on HZSM-5 supported PdO catalyst has been previously reported.

In this study, a DFT study was conducted to investigate methane activation over PdO/HZSM-5 catalyst for methane combustion. Two issues have been considered: (1) the breakage of the first C–H bond in methane over PdO/HZSM-5, which is the rate-determining step for catalytic methane combustion [10,11]; (2) the effect of the support on the catalytic activity. We have previously employed several different cluster models to investigate the structural and electronic properties of PdO/HZSM-5 [18]. Among those clusters, the 7T(6, 1) and 6T clusters correspond to the  $\alpha$ - and  $\beta$ -sites of ZSM-5. The previous investigations confirmed these two sites occupy 85–100% of the total metal sites in the zeolite (ZSM-5, ferrierite and mordenite) [27,28]. In this work, the DFT study was conducted by using only the 7T(6, 1) and 6T clusters. The protonation sites are determined by the Löwenstein rule. The model has been described in detail in our previous DFT study on the interaction between PdO and HZSM-5 support [18].

## 2. Theoretical methods

All the calculations have been performed using the MSI DMol3 program (version 2.2). The double numerical plus polarization (DNP) basis set was used in the calculations to describe the valence orbitals of the atoms. The density functional semi-core pseudopotentials (DSPP) methods were adopted for core treatment. The DFT study was performed with a generalized gradient corrected approximation (GGA) using the PW91 functional [29,30]. During the optimization, methane, PdO and two acidic protons (Ha and Hb) were fully optimized. The transition state was determined by complete linear synchronous transit and quadratic synchronous transit (LST/QST) methods [31]. A LST was performed, followed by repeated conjugate gradient minimizations and QST maximizations until a transition state was located. The atomic charges were calculated using the approach proposed by Mulliken [32].

## 3. Results and discussion

### 3.1. Adsorption of methane molecule on PdO/HZSM-5

Fig. 1 shows the schematic structures of the clusters used to describe methane adsorption. In all the cluster models, methane adsorbs in a bridging mode, i.e., the methane molecule inserts between the oxygen and Pd of PdO with a hydrogen atom pointing toward the oxygen. Further reaction between this hydrogen and PdO represents the activation of methane, as discussed below.

The detailed structural parameters are given in Fig. 2. After methane adsorption, the change in the distance between the Pd atom and the coordinated HZSM-5 framework oxygen atoms is very small. There are also only very slight changes in the distances between protons (Ha and Hb) and the oxygen atom of PdO. After methane adsorption, the Pd–O bond length changes from 1.948, 1.961, 1.965 and 2.166 to 1.950, 1.961, 1.962 and 2.175 Å for the 6T1Al, 6T2Al, 7T1Al and 7T2Al-PdO/HZSM-5

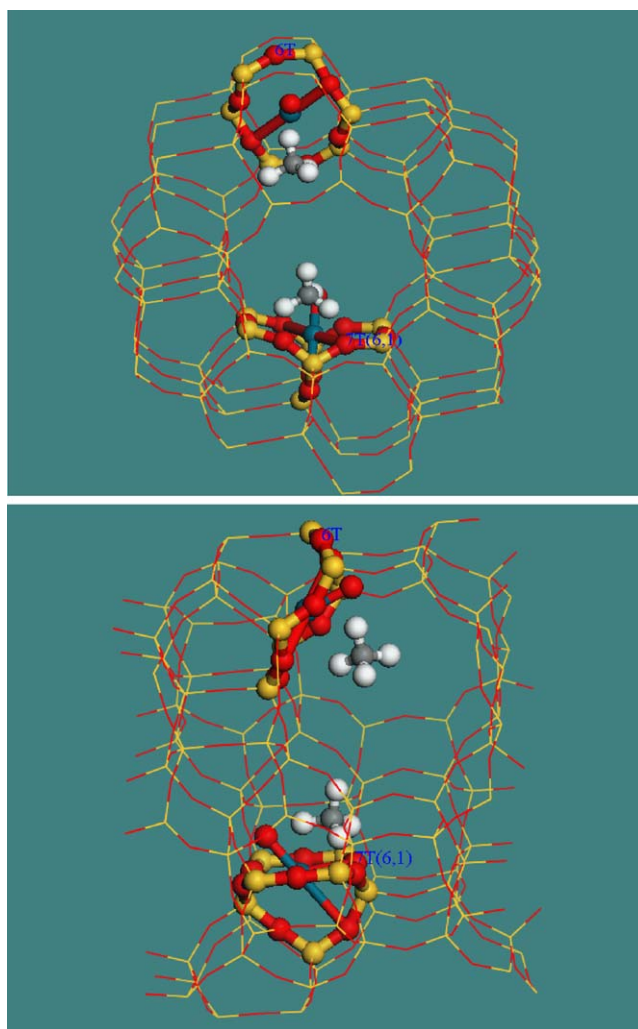


Fig. 1. Schematic structure of the clusters used to describe methane on PdO/HZSM-5 (the balls and sticks represent the clusters and the lines represent the zeolite structure).

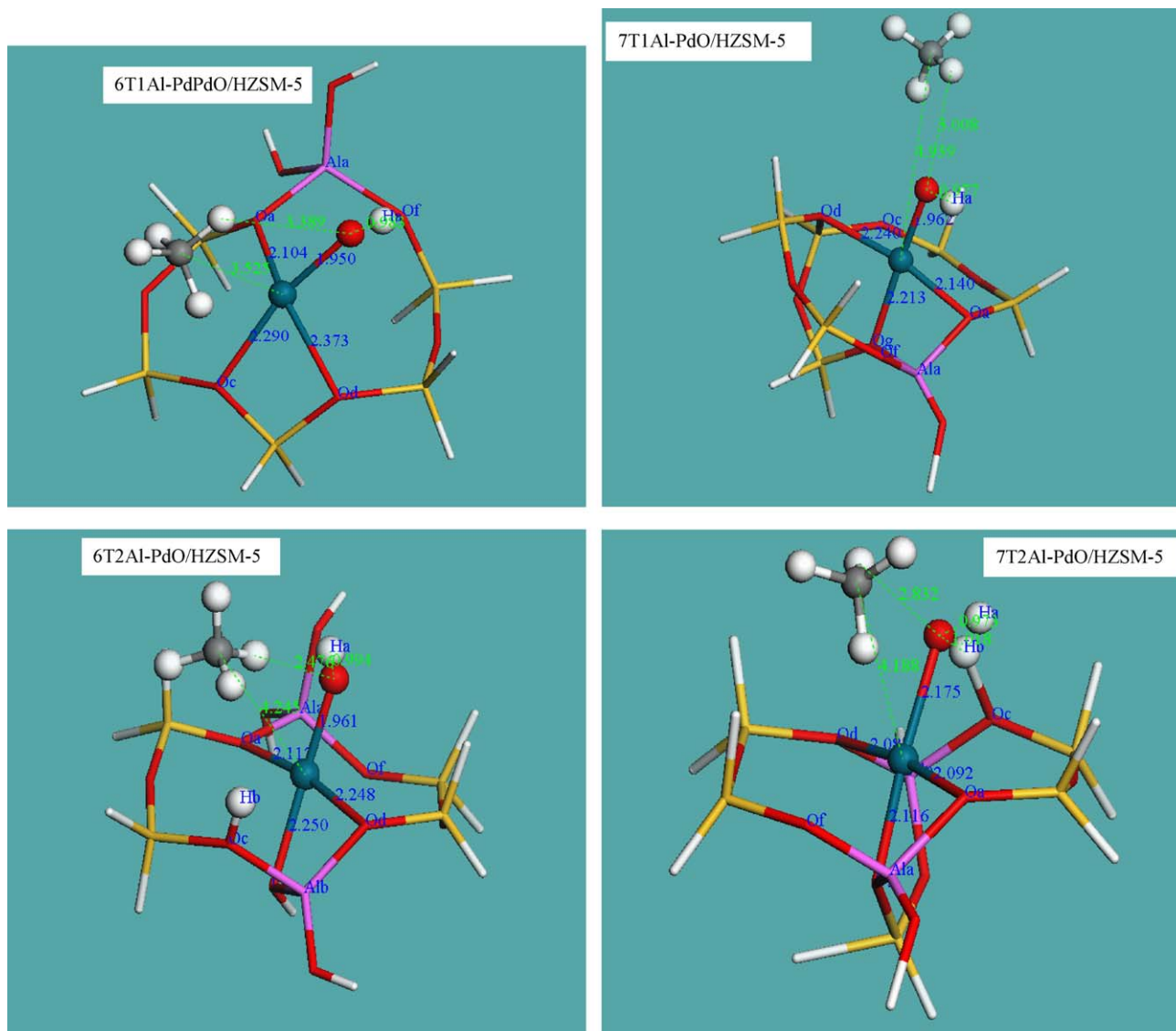


Fig. 2. Geometries of methane adsorption on PdO/HZSM-5 cluster (bond lengths are in Å).

clusters, respectively. The distance between the oxygen atom of PdO and the hydrogen atom in methane molecule, which will be dissociated, is 3.389, 2.476, 3.008 and 2.832 Å for the 6T1Al, 6T2Al, 7T1Al and 7T2Al-PdO/HZSM-5 clusters, respectively. The distance between methane and PdO over 6T2Al and 7T2Al clusters is shorter than that over 6T1Al and 7T1Al clusters. Table 1 shows the Mulliken charge analyses for Pd, oxygen, CH<sub>4</sub>, and Ha or Hb. The changes in charges for Pd, oxygen, Ha and Hb are all very small.

### 3.2. Dissociation of methane molecule on PdO/HZSM-5

The optimized structure for methane dissociation on 6T1Al, 6T2Al, 7T1Al and 7T2Al-PdO/HZSM-5 clusters is shown in Fig. 3. Compared with the initial PdO/HZSM-5 clusters, the local structure of the PdO and the coordination environment of Pd have changes. First, the distances between Pd and the zeolite framework oxygen have more significant changes with 6T1Al and 7T1Al clusters, compared to the changes with 6T2Al and

Table 1  
Mulliken charge analysis for CH<sub>4</sub> on PdO/HZSM-5 clusters

|       | Pd    | O   | CH <sub>4</sub> | H                  |
|-------|-------|---|-----------------|--------------------|
| 6T1Al | 0.614 | Oa -0.841, Oc -0.889, Od -0.862, O -0.552 | 0.012           | Ha 0.315           |
| 6T2Al | 0.511 | Oa -0.849, Od -0.836, Og -0.655, O -0.597 | 0               | Ha 0.334, Hb 0.376 |
| 7T1Al | 0.557 | O -0.554, Oa -0.817, Od -0.872, Og -0.857 | -0.002          | Ha 0.279           |
| 7T2Al | 0.605 | O -0.486, Oa -0.824, Od -0.866, Og -0.795 | 0.003           | Ha 0.295, Hb 0.372 |

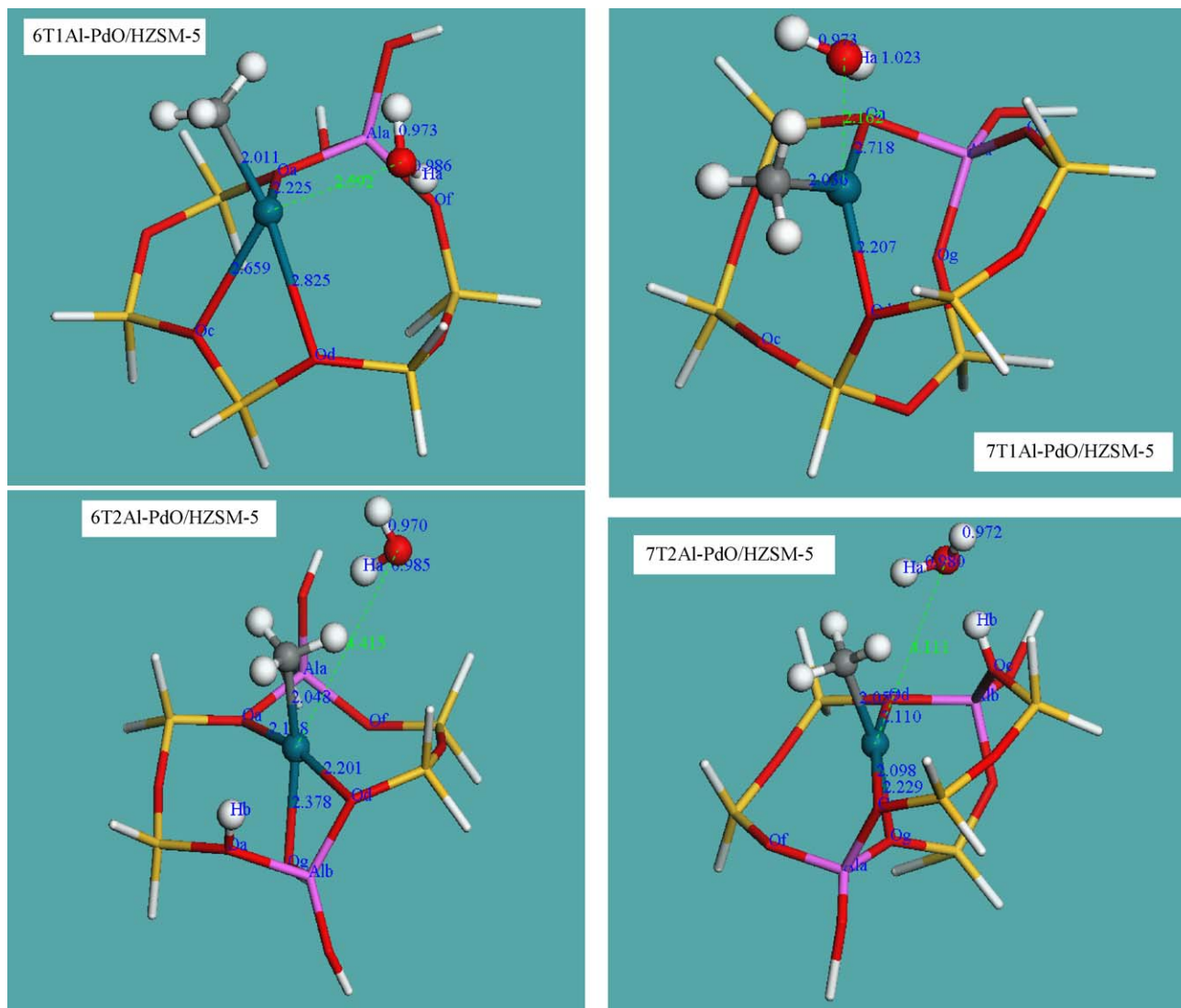


Fig. 3. Geometries of methane dissociation on PdO/HZSM-5 cluster (bond lengths are in Å).

7T2Al clusters. For 6T1Al-PdO/HZSM-5, the distance between Pd and Od or Oc is 2.825 and 2.659 Å, respectively. The Pd–Oa and Pd–Og bond lengths in 7T1Al-PdO/HZSM-5 are 2.718 and 3.154 Å, respectively. For 6T2Al-PdO/HZSM-5 and 7T2Al-PdO/HZSM-5, the distances between the Pd and the framework oxygen atom of HZSM-5 only change slightly. On the other hand, the distance between Pd and oxygen in PdO itself has a more significant change with 6T2Al and 7T2Al clusters. The Pd–O bond distance is 2.592 and 2.162 Å for 6T1Al and 7T1Al-PdO/HZSM-5 clusters, respectively. The distances are larger than the initial values of 1.948 and 1.965 Å. For the 6T2Al and 7T2Al-PdO/HZSM-5 clusters, there is no bond interaction between Pd and the oxygen atom because the distance between Pd and oxygen changed from 1.961 and 2.166 Å initially to 4.415 and 4.111 Å, respectively. This suggests that oxygen in PdO involves in the methane activation directly.

After methane dissociation, it can be seen that a methyl bound to Pd ion and a free H<sub>2</sub>O are produced, as shown in Fig. 3. This suggests too that oxygen in PdO participates in the catalytic reaction, which is consistent with previous experimental

results [8,9]. In addition, Fig. 3 exhibits that the proton in zeolite will participate in the reaction to produce H<sub>2</sub>O molecule. The bond distance between the Pd and the carbon atom of methane is 2.011, 2.048, 2.162 and 2.057 Å over the 6T1Al, 6T2Al, 7T1Al and 7T2Al-PdO/HZSM-5 clusters, respectively. The distance between the dissociated hydrogen and oxygen is 0.973, 0.970, 0.972 and 0.972 Å for the above-mentioned clusters. The oxygen–Ha bond distance is 0.986, 0.985, 1.023 and 0.980 Å for each of the clusters.

The Mulliken charge analyses for Pd, oxygen, H, CH<sub>3</sub>, and Ha or Hb are given in Table 2. The charge of Pd decreases after methane dissociation. The charge of methyl is positive for the clusters containing one Al, whereas that value is negative for those clusters containing two Al.

### 3.3. The transition state geometries and the overall energy diagram

In order to better describe the breaking of the first C–H bond in methane, the transition state (TS) was determined by

Table 2  
Mulliken charge analysis for methane dissociation on PdO/HZSM-5 clusters

|       | Pd    | O   | CH <sub>3</sub> | H                           |
|-------|-------|---|-----------------|-----------------------------|
| 6T1Al | 0.428 | O -0.521, Oa -0.856, Oc -0.876, Od -0.873 | 0.110           | H 0.275, Ha 0.325           |
| 6T2Al | 0.359 | O -0.568, Oa -0.842, Od -0.860, Og -0.662 | -0.003          | H 0.242, Ha 0.302, Hb 0.344 |
| 7T1Al | 0.384 | O -0.487, Oa -0.907, Od -0.889, Og -0.867 | 0.068           | H 0.288, Ha 0.375           |
| 7T2Al | 0.483 | O -0.516, Oa -0.838, Od -0.769, Og -0.892 | -0.143          | H 0.294, Ha 0.299, Hb 0.445 |

complete linear synchronous transit and quadratic synchronous transit (LST/QST) methods [31]. Fig. 4 shows geometries of the transition state structures. In the TS, methane approaches toward PdOH when compared with methane adsorption. The distance between the Pd and carbon atoms is 2.369, 3.004, 2.680 and 3.063 Å, respectively for the TS of methane dissociation over 6T1Al, 6T2Al, 7T1Al and 7T2Al-PdO/HZSM-5 clusters. The Pd–O bond length has been increased to 2.086, 2.574, 2.001 and 2.326 Å for the above-mentioned clusters. For the TS structure over 6T1Al, 6T2Al, 7T1Al and 7T2Al-PdO/HZSM-5 clusters,

the distance between the dissociated hydrogen and carbon is 1.364, 1.567, 1.576 and 1.633 Å, and the distance between the dissociated hydrogen and oxygen is 1.278, 1.504, 1.491 and 1.573 Å, respectively.

The overall energy diagrams for methane adsorption and dissociation over PdO/HZSM-5 are shown in Figs. 5 and 6. All energies are relative to the energy of individual PdO/HZSM-5 and methane molecule. The energy of the methane-adsorbed complex over 6T1Al and 6T2Al-PdO/HZSM-5 is -35 and -37 kJ/mol, respectively. The methane dissociation complex is

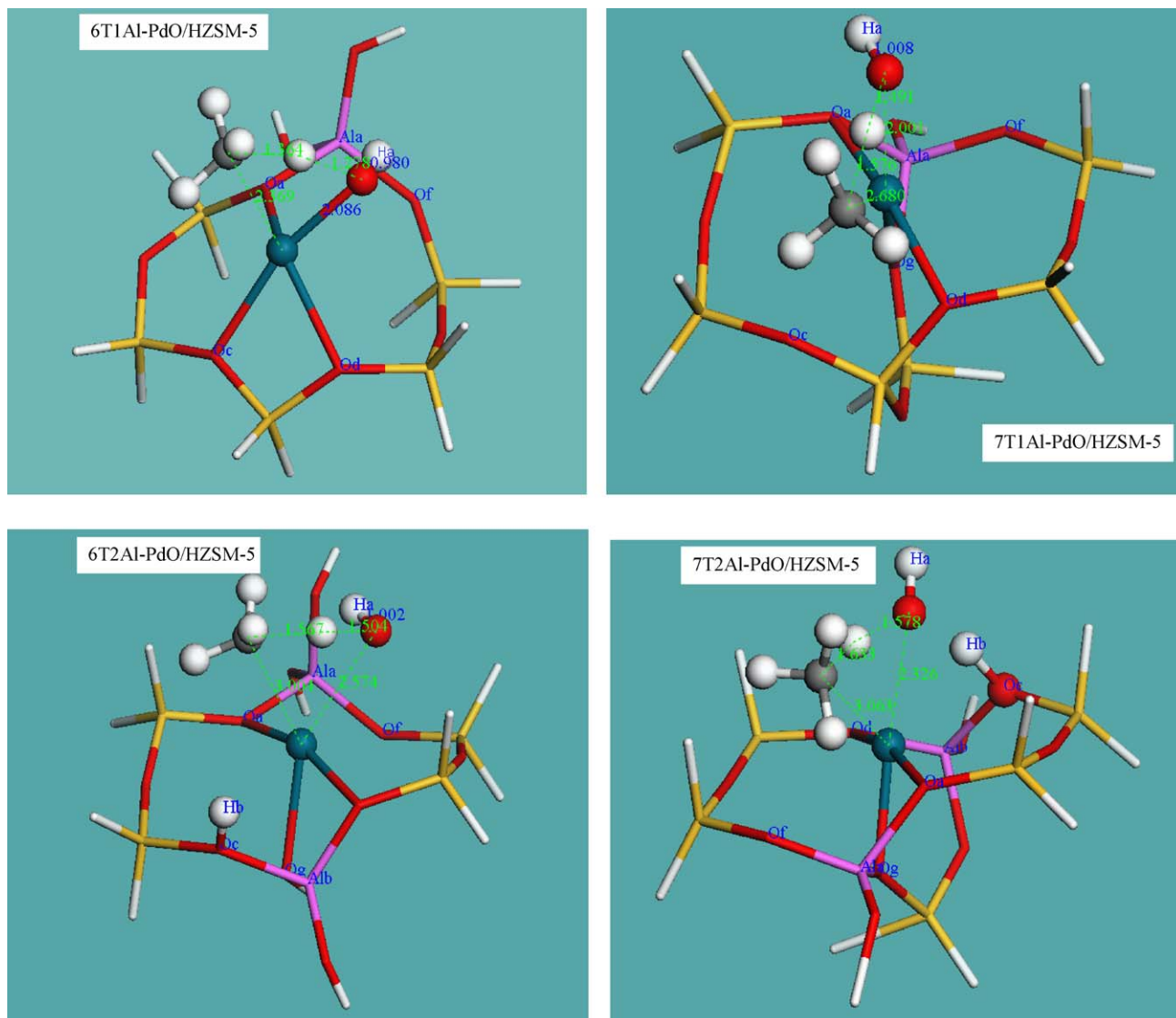


Fig. 4. Geometries of the transition state for the first C–H bond activation of methane (bond lengths are in Å).

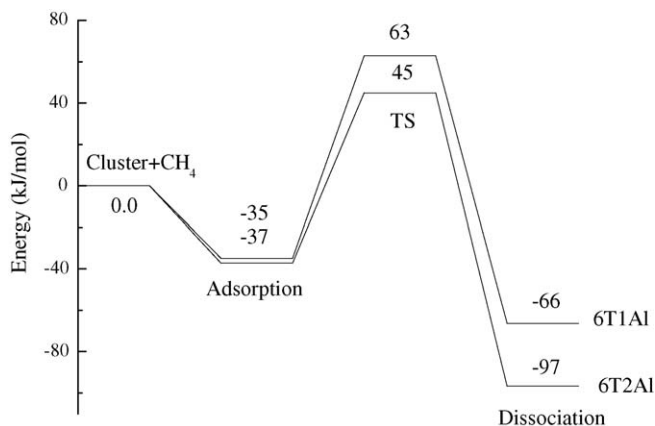


Fig. 5. The energy diagram for the first C–H bond activation of methane on 6T-PdO/HZSM-5.

66 and 97 kJ/mol lower than the reactant in the energy profile for 6T1Al and 6T2Al-PdO/HZSM-5, respectively, while energies of the transition state are 63 and 45 kJ/mol for these clusters. The energy of the methane-adsorbed complex on the 7T1Al and 7T2Al-PdO/HZSM-5 clusters is  $-31$  and  $-40$  kJ/mol, respectively. The dissociation complex is very stable. Its energy is 66 and 93 kJ/mol compared to that of the reactant for the clusters 7T1Al and 7T2Al-PdO/HZSM-5. The energy of the transition state for methane dissociation over 7T1Al and 7T2Al-PdO/HZSM-5 is 63 and 32 kJ/mol higher than the reactant. For 6T1Al, 6T2Al, 7T1Al and 7T2Al-PdO/HZSM-5, the activation energy of methane dissociation is 98, 82, 94 and 72 kJ/mol, respectively. Lyubovsky and Pfefferle have reported that the apparent activation energy for methane oxidation is 67–75 kJ/mol over PdO catalyst [33], while Ribeiro et al. obtained the apparent activation energy of 70–90 kJ/mol when the catalysts reach the stable status [34]. Other investigators confirmed too that the apparent activation energy is ranged from 70 to 90 kJ/mol [35–37]. The activation energies obtained in this work are in good agreement with those previously reported experimental results [33–37].

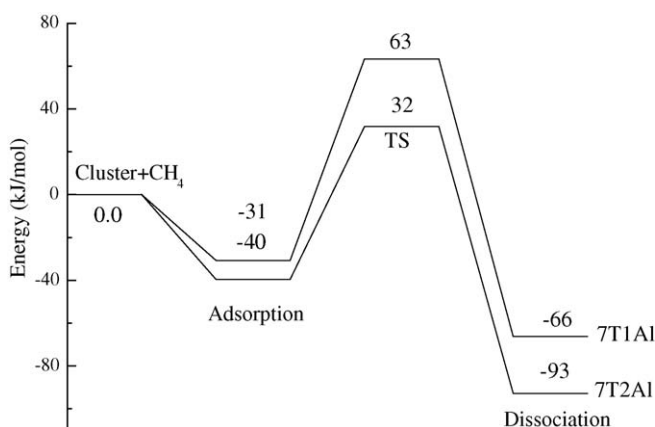


Fig. 6. The energy diagram for the first C–H bond activation of methane on 7T-PdO/HZSM-5.

## 4. Conclusions

The activation of the first C–H bond of methane over PdO/HZSM-5 for methane combustion has been examined by means of DFT study. Within all the cluster models, methane adsorbs in a bridging mode, i.e., the methane molecule inserts between the oxygen and Pd of PdO with a hydrogen atom pointing toward the oxygen. After methane adsorption, the change in the distance between the Pd atom and the coordinated HZSM-5 framework oxygen atoms is very small. There are also only slight changes in the distance between protons (of the zeolite) and the oxygen atom of PdO with methane adsorption. The study shows that both the oxygen in PdO and the proton of HZSM-5 participate in the activation of the first C–H bond of methane. This confirms that PdO is the active Pd species for catalytic methane combustion. The proton in the zeolite promotes the methane activation via the formation of a H<sub>2</sub>O molecule with OH, formed during methane activation over PdO. The activation energies of methane dissociation over 6T1Al and 7T1Al-PdO/HZSM-5 are 97.74 and 94.08 kJ/mol, respectively. The activation energies over 6T2Al and 7T2Al-PdO/HZSM-5 are 16 and 22 kJ/mol less than those over 6T1Al and 7T1Al-PdO/HZSM-5. This suggests that the catalytic activity of PdO can be affected by the acidity of zeolite and more acidic sites would reduce the activation energy for methane activation.

## Acknowledgements

The support from the National Natural Science Foundation of China (under the contract number 20225618 and 20490203) is greatly appreciated. The authors also thank Dr. Jeanne Wynn in the Department of Chemistry of Tianjin University for her excellent work in correcting and improving the usage of English.

## References

- [1] N.K. Labhsetwar, A. Watanabe, T. Mitsubashi, H. Haneda, *J. Mol. Catal. A* 223 (2004) 217.
- [2] C.-J. Liu, K. Yu, Y.-P. Zhang, X. Zhu, F. He, B. Eliasson, *Appl. Catal. B* 47 (2004) 95.
- [3] L.F. Liotta, G. Deganello, *J. Mol. Catal. A* 204 (2003) 763.
- [4] K. Persson, A. Ersson, K. Jansson, N. Iverlund, S. Jaras, *J. Catal.* 231 (2005) 139.
- [5] P. G elin, M. Primet, *Appl. Catal. B* 39 (2002) 1.
- [6] K. Okumura, S. Masumoto, N. Nishiaki, M. Niwa, *Appl. Catal. B* 40 (2003) 151.
- [7] B.H. Yue, R.X. Zhou, Y.J. Wang, X.M. Zheng, *J. Mol. Catal. A* 238 (2005) 241.
- [8] D. Ciuparu, L. Pfefferle, *Catal. Today* 77 (2002) 167.
- [9] D. Ciuparu, E. Altman, L. Pfefferle, *J. Catal.* 203 (2001) 64.
- [10] R. Burch, D.J. Crittle, M.J. Hayes, *Catal. Today* 47 (1999) 229.
- [11] K.-I. Fujimoto, F.H. Ribeiro, M. Avalos-Borja, E. Iglesia, *J. Catal.* 179 (1998) 431.
- [12] C.J. Zhang, P. Hu, *J. Chem. Phys.* 116 (2002) 4281.
- [13] K. Okumura, J. Amano, N. Yasunobu, M. Niwa, *J. Phys. Chem. B* 104 (2000) 1050.
- [14] K. Okumura, J. Amano, M. Niwa, *Chem. Lett.* 997 (1999).
- [15] K. Okumura, W. Niwa, *J. Phys. Chem. B* 104 (2000) 9670.
- [16] L.J. Lobree, A.W. Aylor, J.A. Reimer, A.T. Bell, *J. Catal.* 181 (1999) 189.

- [17] A.W. Aylor, L.J. Lobree, J.A. Reimer, A.T. Bell, *J. Catal.* 172 (1997) 453.
- [18] J.-G. Wang, C.-J. Liu, Z. Fang, Y. Liu, Z. Han, *J. Phys. Chem. B* 108 (2004) 1653.
- [19] C.J. Zhang, P. Hu, *J. Chem. Phys.* 116 (2002) 322.
- [20] H.L. Abbott, A. Bukoski, D.F. Kavulak, I. Harrison, *J. Chem. Phys.* 119 (2003) 6407.
- [21] P. Kratzer, B. Hammer, J.K. Nørskov, *J. Chem. Phys.* 105 (1996) 5595.
- [22] Y. Akinaga, T. Taketsugu, K. Hirao, *J. Chem. Phys.* 109 (1998) 11010.
- [23] E. Broclawik, J. Haber, A. Endou, A. Stirling, R. Yamauchi, M. Kubo, A. Miyamoto, *J. Mol. Catal. A* 119 (1997) 35.
- [24] E. Broclawik, R. Yamauchi, A. Endou, M. Kubo, A. Miyamoto, *J. Chem. Phys.* 104 (1996) 4098.
- [25] G. Tonetto, M.L. Ferreira, D.E. Damiani, *J. Mol. Catal. A: Chem.* 171 (2001) 123.
- [26] D.-Y. Hwang, A. Mebel, *J. Phys. Chem. A* 106 (2002) 12072.
- [27] D. Kaucký, A. Vondrová, J. Dědeček, B. Wichterlová, *J. Catal.* 194 (2000) 318.
- [28] B. Wichterlová, Z. Sobalík, J. Dědeček, *Appl. Catal. B* 41 (2003) 97.
- [29] J.P. Perdew, Y. Wang, *Phys. Rev. B* 45 (1992) 13244.
- [30] J.P. Perdew, Y. Wang, *Phys. Rev. B* 33 (1986) 8800.
- [31] T.A. Halgren, W.N. Lipscomb, *Chem. Phys. Lett.* 49 (1977) 225.
- [32] R.S. Mulliken, *J. Chem. Phys.* 23 (1955) 1833.
- [33] M. Lyubovsky, L. Pfefferle, *Appl. Catal. A* 173 (1998) 107.
- [34] F.H. Riberiro, M. Chow, R.A. Dalla Betta, *J. Catal.* 146 (1994) 537.
- [35] C.F. Cullis, D.E. Keene, D.L. Trimm, *J. Chem. Soc., Faraday Trans.* 67 (1971) 864.
- [36] C.F. Cullis, D.E. Keene, D.L. Trimm, *J. Catal.* 19 (1970) 378.
- [37] T.R. Baldwin, R. Burch, *Appl. Catal. A* 66 (1990) 337.