Applied Surface Science 254 (2008) 5587–5593

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

The cleavage of the methane C–H bond over PdO/H-BEA: A density functional theory study

Yun-xiang Pan, Chang-jun Liu *, Peng Shi

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

ARTICLE INFO

Article history:
Received 2 October 2007
Received in revised form 10 February 2008
Accepted 3 March 2008
Available online 13 March 2008

PACS:
82.75.−z
82.75.Qt
68.43.Bc
31.15.Ew

Keywords:
Zeolite
Palladium
Methane
C–H bond cleavage
Cluster model
Density functional theory

ABSTRACT

Cluster models were used to represent the β-type cationic sites of the protonated beta zeolite (H-BEA) and the loading of PdO on these sites. The properties of these clusters and the cleavage of methane C–H bond over these clusters were studied using density functional theory (DFT) method. The stability of H-BEA was enhanced due to the formation of hydrogen bonds. After PdO loading, the Pd atom bonds to four oxygen atoms among which three H-BEA framework oxygen atoms are included to form an approximate planar structure with Pd in the centre. This structure is very similar to that of bulk PdO. The acidic proton of H-BEA and the oxygen atom of PdO participate in the cleavage of methane C–H bond, indicating that PdO is the active species for the activation of methane. Over the clusters constructed in the present work, the calculated energy barriers for the cleavage of methane C–H bond are in the region between 17.54 and 21.02 kcal mol^{-1}.

1. Introduction

The catalytic combustion of methane has recently drawn more attentions worldwide [1–4]. This process, due to low emission of polluting gases, has been considered to be an excellent candidate for the power generation in gas turbines [3]. Numerous catalysts have been investigated for the combustion of methane [1–8]. However, from the viewpoint of practical application, the catalysts with high activity and durability, such as the palladium–zeolite catalysts, are more attractive.

Beta zeolite (BEA) has a relatively high Si/Al ratio (≥12) and a unique three-dimensional structure with interconnected 12-membered ring channels [9–11]. In the framework of the protonated BEA (H-BEA), there are two types of bridging OH groups: (i) bridging OH groups perturbed by hydrogen bonds, which are usually called perturbed bridging OH groups; (ii) unperturbed bridging OH groups [11]. The Pd/H-BEA catalyst has been found to exhibit excellent performance for the total oxidation of diluted methane in the presence of vapour [8]. Moreover, experimental studies confirmed that the activation of methane C–H bond is the first step for the catalytic combustion of methane over the Pd/H-BEA catalyst [4]. For deep understanding on the catalytic activity of Pd/H-BEA catalyst for the aforementioned reaction and the improvement of this catalyst, theoretical investigation on the cleavage of methane C–H bond over the Pd/H-BEA catalyst is very necessary. In the present work, we aim to investigate this cleavage reaction by using density functional theory (DFT) method.

Before investigating the C–H bond cleavage, we study the loading of PdO on the β cationic sites of H-BEA firstly. In previous experiments [11,12], the β cationic sites with 6-membered rings have been found to be preferable for the location of metal species in the framework of the pentasil ring zeolite. In addition, the β cationic sites are in the wall of the main channel of H-BEA framework, so the metal species locating on these sites are more accessible to reactants and intermediates. Therefore, it can be speculated that the cleavage of methane C–H bond most likely occurs on these sites of the PdO/H-BEA catalyst. There have been a few experimental studies on the PdO/H-BEA catalyst using extended X-ray absorption fine structure (EXAFS) previously

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

0169-4332/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2008.03.003

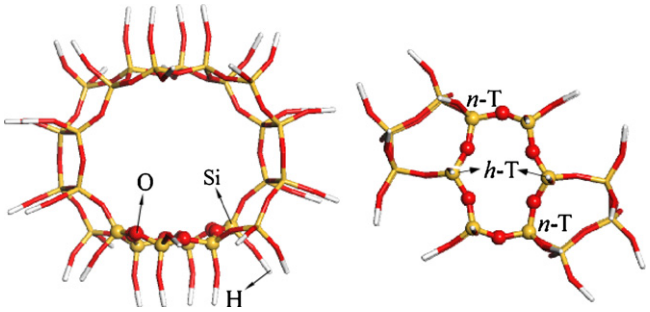

Fig. 1. The cluster model employed to represent the 12-membered ring channel structure of BEA (including 24 SiO_4 tetrahedrons).

[8,13]. EXAFS is a powerful tool for the measurement of metal–oxygen bond distances and coordination number. However, only average values can be obtained using this characterization technique [12]. For this reason, the DFT calculations are useful supplements to the experiments [14,15].

2. Computational models and methodology

2.1. Computational models

The BEA structure, in an all silicon form, was constructed by using a $1 \times 1 \times 1$ unit cell. This unit cell (lattice parameters: $a = b = 12.66$ Å and $c = 26.41$ Å) was taken from the database of Materials Studio (MSI) package of Accelrys [16–18]. A cluster model is employed to represent the 12-membered ring channel structure of BEA and 24 SiO_4 tetrahedrons are included in this model (Fig. 1). In order to generate the H-BEA, one or two Si atoms are replaced by Al atoms and the charge compensating protons are added to the oxygen atoms adjacent to the Al atoms. The position of the β cationic site in the 12-membered ring channel structure is shown in Fig. 1. According to previous studies [19,20] and the rule proposed by Loewenstein [21], four Si atoms could be replaced by Al atoms at the β cationic site, i.e., there are four Al-replacement sites in the six-membered ring. The replacement sites adjacent to the perturbed bridging OH group and to the unperturbed bridging OH group are labelled as *h*-T and *n*-T, respectively, as shown in Fig. 1. In all clusters, the peripheral oxygen atoms are saturated by hydrogen atoms along the framework directions [19,22,23].

The bare clusters are denoted as: *n*-T1Al (with one Al atom and one unperturbed proton); *n*-T2Al (with two Al atoms and two unperturbed protons); *h*-T1Al (with one Al atom and one perturbed proton) and *h*-T2Al (with two Al atoms and two perturbed protons). After PdO loading, the clusters are represented by PdO/*n*-T1Al, PdO/*n*-T2Al, PdO/*h*-T1Al and PdO/*h*-T2Al, respectively.

2.2. Computational methodology

All the calculations were performed with the MSI DMol^3 program from Accelrys [16–18]. A double numerical plus polarization (DNP) basis set was used to describe the valence orbitals of the atoms. The accuracy of the DNP basis set has been analyzed in detail by Delly [18]. The Perdew-Wang (PW91) function of the generalized gradient approximation (GGA) [24,25] was employed to calculate the non-local exchange and correlation energies for all clusters. The convergence criteria were set to 2×10^{-5} Ha, 0.004 Ha Å^{-1} and 0.005 Å for energy, force and displacement convergence, respectively. And a self-consistent-field (SCF) density convergence threshold value of 1×10^{-5} Ha was specified. A Fermi smearing of 0.005 Ha was used to improve the calculation performance. In order to keep the clusters in their positions in the H-BEA lattice, the geometries of all clusters were partially optimized with the peripheral hydrogen atoms fixed to their crystal position. The deformation electron density (DED) was analyzed to demonstrate the electron density depletion of the atoms. DED is defined as the total electron density with the electron density of the isolated atoms being subtracted. The transition states for the cleavage of the C–H bond of methane over the PdO/H-BEA catalyst were determined by the linear synchronous transit (LST) and quadratic synchronous transit (QST) methods [26]. And these transition states were confirmed by the nudged elastic band (NEB) method [27]. Vibrational frequencies analyses were used to determine the nature of the stationary points, i.e., minima (without imaginary frequency) or transition state (with one imaginary frequency).

Following the works of Sauer et al. [22] and Nachtigall et al. [28], the binding energy (BE) is defined as $BE = E^{PdO} + E^{H\text{-}BEA} - E^{PdO/H\text{-}BEA}$, where $E^{PdO/H\text{-}BEA}$, E^{PdO} and $E^{H\text{-}BEA}$ represent the total energies of PdO/H-BEA, the free PdO and bare H-BEA framework, respectively.

3. Results and discussion

3.1. *n*-T1Al, *n*-T2Al, *h*-T1Al and *h*-T2Al

Optimized structures of *n*-T1Al, *n*-T2Al, *h*-T1Al and *h*-T2Al are shown in Fig. 2. The oxygen atoms of the H-BEA framework are denoted as O_1, O_2, O_3, O_4, O_5 and O_6 in all clusters. A proton is bonded to O_1 in *n*-T1Al and *h*-T1Al, and two protons are added in *n*-T2Al and *h*-T2Al, with one bonded to O_1 and the other bonded to O_4. In *h*-T1Al and *h*-T2Al, the protons form hydrogen bonds with the framework oxygen atoms O_3 and O_6, as shown in Fig. 2.

Key structural parameters of *n*-T1Al, *n*-T2Al, *h*-T1Al and *h*-T2Al are summarized in Tables 1 and 2. The calculation results obtained in our present work are consistent with those reported by Fujita et al. [20]. The six-membered ring studied in the present work is distorted somewhat due to the replacement of Si atoms by Al atoms and the addition of the protons, but the main 12-membered ring channel structure of the H-BEA is almost unchanged. Jiang et al. [23] and Demuth et al. [29] have proposed that the Si → Al substitution and the attachment of the proton to the bridging (Si)–O–Al oxygen atom lead to local distortion of the zeolite structure, i.e., the structural distortion occurred only around the replacement site. The relative stabilities of these four clusters are also analyzed. The clusters with one or two perturbed protons are more stable. The electronic energy of *n*-T1Al is 7.11 kcal mol^{-1} higher than that of *h*-T1Al, and the electronic energy of *n*-T2Al is 12.17 kcal mol^{-1} higher than that of *h*-T2Al. The reason for the enhanced stability of *h*-T1Al and *h*-T2Al is simply the formation of the hydrogen bond.

Table 1
Key structural parameters of clusters *n*-T1Al, *h*-T1Al, PdO/*n*-T1Al and PdO/*h*-T1Al

Bond or angle[a]	*n*-T1Al	*h*-T1Al	PdO/*n*-T1Al	PdO/*h*-T1Al
HO_1	0.996 (0.982)[b]	1.003 (1.002)	1.401	1.757
HO_3 (hydrogen bond)		2.004 (1.941)		3.415
AlO_1	2.177	1.907	1.982	1.787
∠AlO_1Si	138.4 (133.5)	135.4 (131.3)	155.8	154.1
HO_p			1.104	1.020
PdO_p			1.903	1.887
PdO_3			2.029	2.237
PdO_4				2.145
PdO_5			2.053	
PdO_6			2.076	2.059

[a] Bond lengths in Å, bond angles in degree.
[b] Bond lengths or angles in parentheses were reported by Fujita et al. [20].