Computational and Theoretical Chemistry 1064 (2015) 7–14

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

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

Enhancing methane dissociation with nickel nanoclusters

H. Seenivasan, Ashwani K. Tiwari *

Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur 741246, India

ARTICLE INFO

Article history:
Received 30 March 2015
Received in revised form 20 April 2015
Accepted 20 April 2015
Available online 1 May 2015

Keywords:
Methane dissociation
Nickel nanoclusters
Size-dependence
Nano catalysis

ABSTRACT

Size dependency of methane adsorption and dissociation on nickel nanoclusters containing 6, 13 and 19 atoms are studied using density functional theory (DFT) calculations. Methane physisorption was identified only on top sites on all the nanoclusters. Elongation of the dissociating C–H bond was found on Ni_6 and Ni_{13} nanoclusters while on Ni_{19} no such elongation was found. Transition state calculations revealed that barrier for methane dissociation on Ni_6 and Ni_{13} clusters are nearly half the barrier for dissociation on Ni_{19} cluster. Comparison of activation energies with this and the previous studies, suggest no geometry dependence i.e., only electronic effect prevails for nanoclusters containing less than ~13 nickel atoms. For smaller nanoclusters (Ni_6 and Ni_{13}) the elongation of the dissociating C–H bond in the adsorbed state acts as the precursor state for dissociation, thereby reducing the energy barrier for methane dissociation. However, no sign of precursor formation is observed in the case of Ni_{19} nanocluster and hence a large barrier. Semi-classical dissociation probability plots show high dissociation probabilities for Ni_6 and Ni_{13} nanoclusters compared to Ni_{19} clusters and low-indexed nickel surfaces.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Catalysis by metal nanoparticles of size lying between the bulk metal and molecules is termed nanocatalysis. Heterogeneous catalysis using these nanoparticles is of recent interest owing to the size and shape dependency of catalytic properties. Industrial applications of nanoparticle catalysts include and not limited to fuel cells, exhaust catalysts, gas sensors, photocatalysts, enantioselective catalysts etc. [1–3]. Remarkable variation in reactivity is reported for nanoparticles less than 2 nm [4–6]. Two major reasons for nanoparticles showing different properties than bulk are surface and quantum size effects. Size induced metal–insulator transition in metal nanocrystals occurs in the range of 1–2 nm diameters [5]. It is also found that as the cluster size decreases, the Kubo gap increases and the density of states near the Fermi level decreases. This leads to the small clusters to behave like atoms and molecules with discrete density of states (DOS) in contrast to the band structure of the larger clusters and bulk metals. Size dependent effects are of two kinds, viz., non-scalable ones which relate to fraction of atoms at surface, where we see non-monotonic trends with increasing number of atoms and quantum effects due to complete filing of shells, showing discontinuous behavior for certain clusters [6]. It has been well documented that in addition to their magnetic and electronic properties, small transition metal clusters exhibit strong size dependent variations in their catalytic behavior and this behavior is different for different metals. Electronic finite size effects vanish beyond 1.6 nm in the case of platinum and it converges to bulk more quickly than gold [7–9]. Due to partially filled d-states providing high density of states around Fermi level, quantum size effects were not observed in Pt clusters. In literature, there have not been many systematic theoretical studies on the size dependent catalytic activity till date. However, for many reactions, reduction in the activation energy is found on step surfaces compared to the close packed surfaces exhibiting the geometrical effect. Similarly, for nanoparticles, step density and hence the reactivity can be controlled with changing the size [10].

Steam reforming process, an important industrial reaction, produces hydrogen and synthesis gas. This reaction is performed at high temperature and pressure and these conditions render deactivated nickel nanoclusters [11]. Recent experiments and calculations were able to provide an atomic picture of this reaction. Two kinds of active sites were found to be crucial in describing the steam reforming process on supported Ni-nanoparticles: highly active defect sites and the less active close packed sites [12,13]. It has also been identified that methane activation is an example for a positive size-sensitive reactions in which turnover frequency increases with decreasing particle size. van Santen in his review classifies methane dissociation as a reaction which depends on the coordinative unsaturation and suggested that the rate will increase with decreasing particle size [14]. Different

---

* Corresponding author. Tel.: +91 7890468482; fax: +91 33 2587 3028.
E-mail address: ashwani@iiserkol.ac.in (A.K. Tiwari).

http://dx.doi.org/10.1016/j.comptc.2015.04.016
2210-271X/© 2015 Elsevier B.V. All rights reserved.

classes of reactions have different active sites and different dependence of catalytic activity on particle size. Analysis of transition state geometries of CH_4 dissociation on various metals found a weak structural effect in the case of C–H bond breaking where the electronic effect dominates over geometrical effect in deciding the barrier for dissociation [15].

Only a few previous reports are available on methane dissociation on supported and un-supported nanoclusters [16–20] compared to a large literature on metal surfaces [21–34]. Earlier combined experimental and theoretical study by Trevor et al., showed size dependence of reactivity for methane dissociation on unsupported Pt clusters. They reported a non-monotonic change in reactivity with size up to 24 atoms, while the overall reactivity tends to decrease with increasing cluster size [16]. It was suggested that details of electronic structure and geometry maybe important in deciding the reactivity and low-coordination metal atoms activate methane more readily than the closely packed surface atoms. Recent DFT calculations using PW91 functional on CH_4 dissociation on Ni_4 (tetrahedral) and Ni_{13} (icosahedral) clusters reported lower barriers compared to that on Ni(1 1 1) surface [17]. Very recently, Vines et al. [18] and Cheng et al. [19,20] reported an enhanced catalytic activity of Pt nanoparticles/clusters in methane dissociation. Former highlighted the effect of edge and corner sites of nanoparticles in improving methane activation compared to surfaces while the latter showed the shape and support effect on this reaction on platinum nanoparticles.

As discussed above, few studies in literature report methane dissociation on Pt clusters while that on Ni clusters is scarce. This evokes the need of atomic level understanding of physical and chemical process taking place on nickel nanoclusters. Nickel was the choice of this study for it being industrially relevant and a late-transition element exhibiting many accessible oxidation states and weak not very reactive metal–carbon bonds which would make them a better catalyst. We, in this study, investigate in detail, the size dependence of methane adsorption and dissociation on sub-nanometer size nickel nanoparticles/clusters less than 1 nm diameter where the size dependence is found to be predominant and compare them with the results obtained on single crystal surfaces. Aim of the present study is to reveal the mechanism of the size dependency of the dissociation of methane on nanoclusters.

2. Methods

Nanoparticles may have various shapes depending upon the method of synthesis, but spherical shape is widely encountered which can be modeled as polyhedra like icosahedron and cubo-octahedron in order to minimize surface energy [1]. The cubo-octahedral clusters provide a convenient model for studying the correspondence between cluster surface properties and the properties of certain bulk surfaces. On every cluster triangular face is similar to close-packed (1 1 1) and an edge corresponds to (2 1 1) slab [7–9]. We, in this study, have assumed the cubooctahedron shape for the nanoparticles. Nanoclusters (NCs) were modeled as metal clusters within a supercell with periodic boundary conditions. Vacuum space of ~10 Å was used to avoid interaction with adjacent clusters. Total energy DFT calculations were performed by using Vienna *ab initio* simulation package (VASP) code [35–38]. Plane wave basis set with Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional within the generalized gradient approximation (GGA) was employed to treat nonlocal exchange–correlation effects [39,40]. Projector augmented-wave (PAW) potentials were used to describe the interactions between the ionic cores and electrons [41,42]. $1 \times 1 \times 1$ Γ-centered grid of *k*-points sampled the Brillouin zone for structure optimization. Spin-polarized calculations have been performed with plane wave expansion truncated at 400 eV. Structure optimization and adsorption energy calculations are considered converged when all forces are smaller than 0.01 eV/Å. Charge density difference (CDD) plots were obtained by calculating difference between the charge of the adsorbed system and the sum of the isolated adsorbate and nanocluster, where the atomic positions are fixed as those they have in the adsorbed system using the VESTA software [43]. Transition states were identified by climbing image-nudged elastic band (CI-NEB) method [44]. For transition state calculations, convergence criterion is when the forces are less than 0.02 eV/Å. Vibrational frequencies at the transition states were calculated to confirm that the TS obtained is a first-order saddle point. Adsorption energy, E_{ads} is defined as $E_{ads} = E_{(adsorbate\ +\ NP)} - [E_{(adsorbate)} + E_{(NP)}]$, where $E_{(adsorbate\ +\ NP)}$, $E_{(NP)}$, and $E_{(adsorbate)}$, are energies of the adsorption system, nanoparticle, and gas phase molecule, respectively. Only high symmetry adsorption sites as shown in Fig. 1 were used in this study.

3. Results and discussion

3.1. Nanocluster optimization

Nanoclusters containing 6, 13 and 19 nickel atoms corresponding to particle diameters of 0.4, 0.6 and 0.7 nm assuming a quasi-spherical structure were used in this study. Recent findings in the sub-nanometere size regime as discussed in the introduction section is the motivation for studying nanoclusters of size less than 1 nm diameter. Octahedral (and cubo-octahedral) shapes and *fcc* arrangement with *Oh* symmetry is assumed for all clusters. Details of the structures are given in Table 1. Calculated average coordination numbers of surface atoms of Ni_6, Ni_{13} and Ni_{19} clusters are 4, 5 and 6 respectively which increases with increasing size of the nanocluster. These coordination numbers are very low compared to those seen on the single crystal surfaces. Binding energy per atom, E_B is calculated as $E_B = [E_T - nE_{atom}]/n$, where, E_T is the total energy of the cluster, E_{atom} is the energy of the single Ni atom and n is the number of Ni atoms in the cluster. Binding energy was found to increase with increase in the size of the cluster. Average Ni–Ni distance in the nanoclusters increases with the number of Ni atoms in the cluster increases. On increasing the size of the particles this value may reach the equilibrium Ni–Ni distance of 2.49 Å found on surfaces. Non-convergence of binding energy per atom and bond lengths to bulk values shows that these clusters are still in the non-scalable regime of properties. Similar increase in the average metal–metal distance, binding energy per atom and variable Ni–Ni distance with increasing particle size was previously reported in Ni, Pt and Pd clusters [45–48].

3.2. CH_4, CH_3 and H adsorption and co-adsorption

All calculations were performed with the metal cluster atoms fixed at their optimized positions and the adsorbing molecule relaxed on the desired adsorption site. As the barriers for direct reaction from gas phase have been carried out, the lattice relaxation of the heavy metal atoms is slower and induces only minor changes. Moreover, it was shown that for O and CO adsorption on Au metal nanoparticles that relaxing metal atoms during adsorption had a negligible geometrical effect [7]. Methane, methyl and hydrogen adsorption on various sites on the three nanoclusters were studied. It was found that, on all the three NCs, methane preferably adsorbs only on the top site with adsorption energies of −0.15, −0.20 and −0.11 eV, respectively and there is no adsorption on any other sites (Table 2). Adsorption energies of methane

Download English Version:

https://daneshyari.com/en/article/5393273

Download Persian Version:

https://daneshyari.com/article/5393273

Daneshyari.com