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Full Length Article

Capability of defective graphene-supported Co_4 nanoparticle toward ammonia dehydrogenation

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ABSTRACT

Performing density functional theory calculations, we have studied the adsorption of nanoparticle Co_n (n = 2, 4, 6) on graphene sheets and Co_4 stands out for the most favorable stability. Furthermore, the catalytic activity of Co_4-supported on a variety of graphene sheets was explored toward ammonia dehydrogenation. Present results demonstrate that the existence of C-vacancy in graphene considerably enhances the interaction of NH_x (x = 3–0) with Co_4 cluster, and effectively facilitates H abstraction from ammonia. Specifically, Co_4 anchored on monovacancy graphene sheet outperforms the others for its superb catalytic activity in NH_3 decomposition, giving rise to the intermediates NH and/or N bound with the nanocomposite. In contrast, doping of N or B atom in graphene hinders the N—H bond cleaving of NH_3. The higher catalytic activity of Co_4 supported over the vacancy graphene is correlated well with the lower d-band center value relative to the Fermi level, consistent with the literature emphasizing on the importance of support to metal catalysts.

1. Introduction

The emergence of graphene has opened an exciting avenue for utilizing 2D carbon material as a support of nanoparticle catalysts, owing to the large surface area, outstanding electrical conductivity and excellent structural stability [1,2]. Great endeavor has devoted to these metallic nanoclusters i.e. Pt [3–9], Pd [10–13], Au [6,14], Fe [15] adsorbed on graphene sheets, which act as catalysts in various reactions like CO and methanol oxidation, oxygen reduction reaction, and methanol decomposition.

As addressed in the literature, pristine graphene (PG) with relatively inert property, makes metal clusters adsorb weakly and diffuse easily, leading to their sintering eventually [16,17]. In contrast, it has been well elaborated that the vacancy sites in graphene sheets, which are unavoidable in the synthesis or induced by specific experimental strategies [18], are responsible for anchoring metal nanoparticles, inhibiting their sintering, further to improve their stability and reactivity [3,6,10]. For instance, the activation barrier of CO oxidation catalyzed by Au_8, Pt_n (n = 4, 13) supported on vacancy-graphene sheets [3,6] is greatly reduced relative to that on PG, and the reactivity is enhanced accordingly. Similar cases have been reported for Pd_{13} and Pt_{13} anchored on monovacancy [10] and divacancy graphene [7] sheets (abbreviated as SVG, DVG thereafter), respectively. Alternatively, doping of heteroatom in graphene can also alter the catalytic performance of the supporting metallic nanoparticles by modifying the interfacial interactions [5,15]. As evidenced in the literature [5] that Pt_{13} supported on N-doped graphene exhibits super catalytic reactivity toward oxygen reduction reaction.

Noteworthily, graphene-supported cobalt nanoparticles, commonly used as catalysts in Fischer-Tropsch synthesis (FTS), display excellent catalytic performance, i.e. high activity and selectivity, long-term stability, and great resistance to sintering [19–21]. Presently, cobalt clusters, both in free-standing [22–25] and adsorbing on graphene sheets [26–30] have been intensively explored to unravel their novel properties for applications in nanoelectronics and electrochemistry. So far, the stability, electronic and magnetic properties of sub-nanoparticles Co_n (n = 2–4, 13) [26–30] adsorbed on pristine graphene have been evaluated mostly at the level of density functional theory (DFT) calculations. However, the adsorption of small cobalt clusters on defective graphene sheets is yet to be characterized, and it is intriguing how the catalytic capability of Co cluster is tailored by various defective graphene substrates.

Herein, a series of DFT calculations have been conducted to evaluate the properties of small Co_n (n = 2, 4, 6) clusters adsorbed on PG, SVG and DVG sheets firstly, and Co_4 stands out as the most stable one of them. Owing to the poisoning of ammonia on cobalt-based catalytic in FTS [31–33], we thus have explored the adsorption and dehydrogenation of ammonia on Co_4 anchored on various graphene supports,

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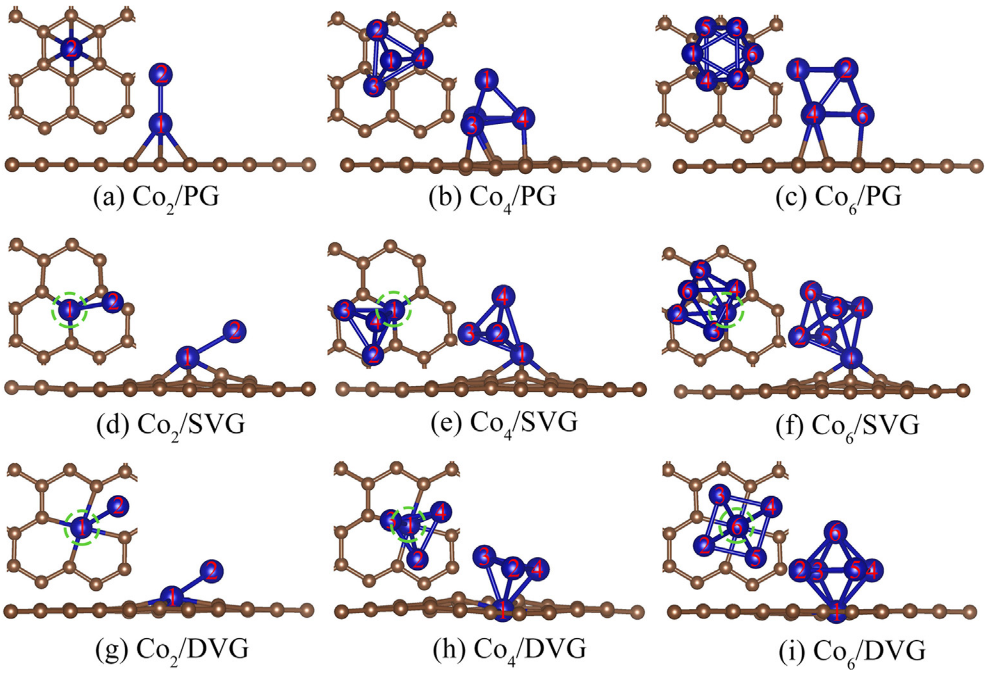

Fig. 1. Top and side views for the optimized geometrical structures of Co_n (n = 2, 4, 6) adsorbed on PG (a–c), SVG (d–f) and DVG (g–i), respectively. (Color map: gold-–carbon, blue–cobalt; the green dashed circles denote the vacant sites in graphene sheets). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

including PG, SVG, DVG, heteroatom B and N embedded in the vacant site of SVG (abbreviated as Co_4/PG, Co_4/SVG, Co_4/DVG, Co_4/B-G, Co_4/N-G thereafter, respectively), to make clear the effects of supports on the catalytic activity of Co_4. Moreover, the catalytic activity was well correlated with the metal cluster *d*-band center. Present results predict that Co_4 anchored on vacancy graphene, especially on SVG, outperforms the other cases with its superior capability toward ammonia dehydrogenation.

2. Computational details

All spin-polarized DFT calculations were performed with projector-augmented wave (PAW) [34] potentials as implemented in the Vienna Ab-initio Simulation Package (VASP) [35]. The electron exchange and correlation interactions were described within the generalized gradient approximation of the Perdew, Burke, Enzerh (GGA-PBE) functional [36]. A kinetic energy cutoff was set as 450 eV, and present calculated lattice constant for graphene (2.47 Å) compares well with available experimental value [37] and other DFT calculations [38,39].

A supercell of 4 × 4 × 1 was adopted to simulate monolayer graphene, along with a vacuum layer of 15 Å. The monovacancy and divacancy graphene sheets were constructed by removing one or two adjacent carbon atom(s) in pristine graphene. For geometrical optimization, the Brillouin zone (BZ) [40] integration was performed with a Γ-centered Monkhorst-Pack (MP) grid of 7 × 7 × 1, and all atoms were fully relaxed until the forces were less than 0.02 eV/Å. A Γ-centered MP grid of 15 × 15 × 1 was used for electronic density of states (DOS) calculations.

The binding energy (E_b) of Co_n (n = 2, 4, 6) adsorbed on graphene sheets (denoted as Co_n/Gra) is computed by Eq. (1),

$$E_b = (E_{Co_n} + E_{Gra}) - E_{Co_n/Gra} \tag{1}$$

where E_{Co_n}, E_{Gra} and $E_{Co_n/Gra}$ are the total energies of free Co_n cluster, graphene sheets without and with Co_n adsorbed, respectively. The adsorption energy (E_{ad}) of NH_x (x = 0–3) species over the Co_n/Gra nanocomposites, was defined with Eq. (2),

$$E_{ad} = \left(E_{NH_x} + E_{Co_n/Gra}\right) - E_{NH_x-Co_n/Gra} \tag{2}$$

where $E_{NH_x}$and $E_{NH_x-Co_n/Gra}$are the total energies of free NH_x (x = 0–3) species and NH_x (x = 0–3) adsorbed on the Co_n/Gra, respectively. Positive values of E_b and E_{ad} indicate an exothermic adsorption.

Bader charge analysis [41] was utilized to evaluate the electron charge transfer between the adsorbate and substrate. For ammonia dehydrogenation, the climbing image nudged elastic (CI-NEB) method [42] was used to search the reaction transition state (TS) and to estimate the activation energy of N−H bond cleaving. Frequency analysis was performed to ensure that there is no imaginary frequency for the stable initial (IS) and final states (FS), while there is a single imaginary one for the TS state.

3. Results and discussion

First for free Co_n clusters, the linear dimer (Co_2), tetrahedron and planar tetramer (Co_4), hexamer (Co_6) with four configurations of octahedron, triangular prism, capped square pyramid and pentagonal pyramid were taken into consideration, and the optimized structures, calculated formation energies are shown in Fig. S1. It is found that the linear Co_2, distorted tetrahedron Co_4 and regular octahedron Co_6 are energetically the most favorable structures. Correspondingly, the averaged Co−Co bond lengths and formation energies are 1.96 Å and 1.53 eV/atom for Co_2, 2.33 Å and 2.34 eV/atom for Co_4, 2.27 Å and 2.99 eV/atom for Co_6, which compare well with the experiments (Co_2:1.6–2.3 Å and 0.7–1.4 eV/atom) [43] and theoretical calculations (Co_2:1.96 Å and 1.45 eV/atom, Co_4: 2.34 Å and 2.27 eV/atom, Co_6:2.27 Å and 2.93 eV/atom) [25].

As for the adsorption of Co_n on supports, the high symmetrical adsorption sites were examined to determine the most favorable configurations of Co_n, such as top (T), bridge (B) and hollow (H) sites of hexagonal-ring on PG, vacant site on SVG and the center of divacancy on DVG. Meanwhile, two contact ways of parallel and perpendicular to graphene sheet were considered for the molecular orientations, e.g. (1) top-down point contact, where one of the Co atoms is placed at symmetrical positions; (2) facet-down triangle contact, which one center of tetrahedral or octahedral facet was laid at symmetrical positions.

3.1. Adsorption of Co_n (n = 2, 4, 6) on graphene sheets

To clarify the interaction of cobalt clusters with graphene supports, the geometries, stability and electronic structures were discussed for the most favorable structures of Co_n (n = 2, 4, 6) adsorbed on PG, SVG and