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Reactivity of CO on Ni_4 cluster- effect of spin multiplicity and H doping-A DFT investigation

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ABSTRACT

We investigated the reactivity of carbon monoxide on tetrahedral Ni_4 clusters at different spin multiplicity applying density functional theory calculations considering pure and hybrid functional. The stability of the clusters increases with the increasing spin multiplicity and doping hydrogen in Ni_4 cluster. The adsorption or binding energy of CO on Ni_4 cluster is thermodynamically feasible process at normal condition whereas dissociation is not feasible. Ab initio molecular orbital analysis shows the orbital overlaps are observed at bridging site, three fold sites, and tetra coordinated centre and formation of δ-bond in the cluster. In NBO analysis, CO binds strongly to the Ni_4 cluster not only by two Ni—C bond (spd hybrid), but also donor-acceptor delocalization interactions, for example, σ type BD(C—O) → BD*(Ni—C) and BD(Ni—C) → BD*(Ni—C/C—O), two π-type BD(C—O) → LP*(Ni) and several diffuse RY*(C) ← LP(Ni) and π*(CO) ← LP(Ni) interactions. Singlet Ni_4 cluster shows highest activation energy barrier, 3 eV. H-doped Ni_4 cluster decreases dissociation barrier and favors C—H bond formation.

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1. Introduction

The investigation of the reactivity of CO on metal catalysts, both on surfaces [1] and clusters [2] are an intense area of research throughout the decades for its tremendous industrial applications, viz. for the synthesis of carbon nanotubes [3–5], purification of hydrogen [6, 7] and production of synthetic natural gas(SNG) like methane [8, 9]. CO prefers to bind three fold sites of fcc and hcp on Ni (111) surface, both experimentally [10, 11] and theoretically [12, 13], whereas few spectroscopic studies [14, 15] identified that CO binds on bridging two fold sites. Pavao et al. [16] calculated the adsorption and dissociation energies of CO on transition metal surfaces, and Nakano et al. [17] observed the deposition of carbon at 400 K by scanning tunneling microscopy (STM) on stepped Ni (111) surface.

Although Ni catalysts or alumina supported Ni catalysts are low cost and higher reactivity, the dissociation energy barrier for CO is very high. The thermo gravimetric decomposition of CO on supported Ni catalyst in temperature range 280–400 °C [18]. Recently, kinetic of methanation of CO over Ni/γ-Al_2O_3 studied experimentally high pressure 16 bar and temperature, 443–473 K [19]. Recently, Wang et al. [20] investigated dissociation and methanation of CO on Ni_4/γ-Al_2O_3 and Ni_3Fe/γ-Al_2O_3 and observed the dissociation barrier for CO is 3.19 eV and 2.21 eV, respectively. They discussed that the presence of hydrogen lowers the dissociation barrier. But the reason behind the higher dissociation barrier and effect of hydrogen to lower the barrier is still to be understood. Hu et al. [21] investigated the interaction of CO and CO_2 on Ni_2 cluster applying DFT methods. Anderssona et al. [22] observed that CO dissociation on Ni surface through COH species on step sites. Moreover, Iglesia et al. [23] investigated that CO hydrogenation on Fe (110) and Co (0001) surface are activated by hydrogen.

Nowadays, investigations on small sized clusters and their catalytic application are increasing due to their better reactivity than bulk sized catalysts [24–27]. Arvizu et al. [28] and Goel et al. [29] determined structural properties, binding energies, and adiabatic ionization potentials at different spin multiplicities (singlet, triplet, quintet, septet and nonet) for Ni_{2-5} clusters applying DFT methods. Petkov et al. [30] identified the effect of impurity atoms carbon and oxygen on the geometry, stability, electronic and magnetic properties, ionization potential and electron affinity of Ni_4 cluster of tetrahedral structures with T_d, C_{3v}, C_{2v}, C_s symmetries and planar structures with C_{2v} and D_{4h} symmetries. They reported that C_s is the most stable geometry for tetrahedral Ni_4 cluster, and due to Jahn-Teller distortion T_d symmetry is destroyed. Furthermore, Xie et al. [31] calculated the structural and magnetic properties of Ni_{2-13} clusters and observed that high-symmetry clusters are unstable due to Jahn-Teller distortion, possessing multiple degeneracy.

However, the catalytic activity of clusters depend on viz., surface to volume ratio, adsorption energy and adsorption sites, energy barriers, coordination numbers and also constituent atoms. Though several studies had been reported on the effect of spin on the physical properties of Ni clusters, but till now the effect of spin multiplicity on the adsorption and dissociation of CO molecule is not investigated.

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In this work, we introduced the effect of spin multiplicity on the properties like binding energy, geometry, global hardness, ionization potential, electron affinity, dipole moment and vibrational frequencies for tetrahedral Ni_4 clusters, and the molecular orbital interaction between CO and Ni_4 cluster at different multiplicity is discussed to understand the adsorption applying DFT methods. The adsorption or binding energy, dissociation energy, Gibbs free energy, and activation energy barrier is calculated. How the dissociation energy or activation energies are affected in presence of H atom in the Ni_4 cluster is also explained by molecular orbital interaction.

2. Computational Details

We optimized the geometries of singlet, triplet, quintet, septet and nonet Ni_4 clusters, and subsequent frequency calculations have been carried out at the generalized gradient approximation(GGA) [32] using Perdew-Burke-Ernzerhof (PBE) [33] exchange correlation functional and hybrid functional PBE1PBE with the aid of Gaussian 09 W package [34]. The molecular geometries are represented applying Gauss View package [35]. We used mixed basis sets, for example, LANL2DZ (for Ni) and 6-311+G(2d,2p) for C, O and H in pure PBE functional; and LANL2MB (for Ni) and 6-311+g(3df,3pd) for C and O in hybrid PBE1PBE functional. The scalar relativistic effective core potentials of LANL2DZ and LANL2MB are used for the core electrons in Nickel. The global hardness [36] is defined as the energy gap of HOMO and LUMO, thus $\eta =$ HOMO-LUMO, where HOMO stands for highest occupied molecular orbital and LUMO stands for lowest unoccupied molecular orbital. The ΔSCF method is used to calculate ionization potential (IP) and electron affinity (EA). 'Pop = nbo' option is used for natural bonding orbital calculation.

The binding or adsorption energy (E_b) of CO on the cluster is calculated from, $E_b = E_{Ni4/CO}- (E_{Ni4} + E_{CO})$, where $E_{Ni4/CO}$, E_{Ni4}, and E_{CO} are electronic energies for adsorption configuration, bare cluster, and isolated CO, respectively. The dissociation energy (E_{diss}) is defined as the subtraction between the energies of dissociated state (E_{DS}) and the sum of energies for bare cluster ($E_{cluster}$) and isolated CO, $E_{diss} = E_{DS} -(E_{cluster} + E_{CO})$. The Synchronous Transit-Guided Quasi-Newton (STQN) [37] methods are used to determine TS geometry. The electronic energy barrier, $E_{Act} = E_{TS} - E_{IS}$, where E_{TS} and E_{IS} are energy of the transition state and initial state, respectively.

Calibration of the computational methods are done by comparing theoretically calculated bond distance of Ni_2 cluster and CO with available experimental data, for example, Ni—Ni bond distance is 2.123 Å in PBE functional and 2.172 Å in hybrid PBE1PBE functional, (Experimental bond distance is 2.1545 Å [38]), and for CO, the calculated bond distance is (1.1256 Å) in PBE/6-311+G(2d,2p) method and (1.1229 Å) in PBE1PBE/311+g(3df,3pd) method (Experimental bond distance 1.13 Å [39]).

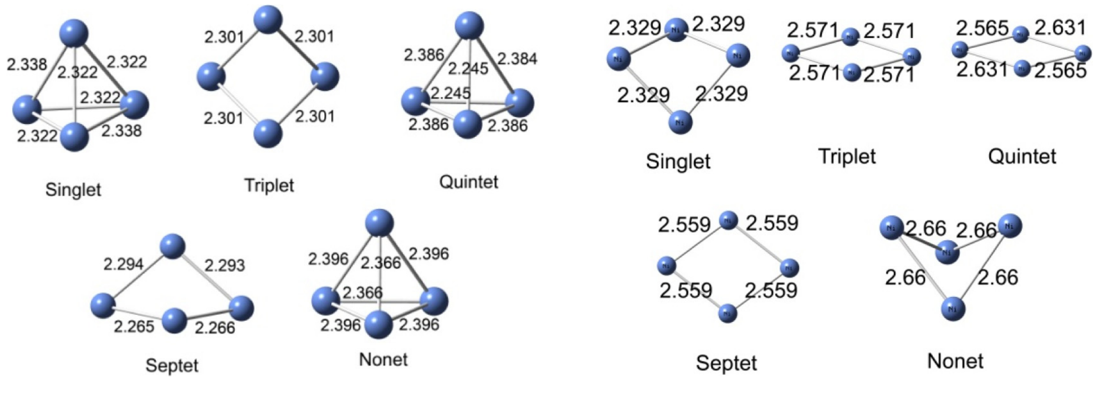
3. Results and Discussion

3.1. Geometry and Properties of the Ni_4 Cluster at Higher Multiplicity

The variation of the geometries of the Ni_4 cluster at different multiplicity states are shown in Fig. 1, and their properties, viz. binding energy, chemical hardness, ionization potential, electron affinity, dipole moment and vibrational frequencies are represented in Table 1. Both the pure PBE and hybrid PBE1PBE functional calculations show that stability increases with increasing multiplicity. The calculated BEs for tetrahedral Ni_4 cluster at different spin states are 4.31 eV, 4.37 eV, 4.56 eV, 4.39 eV and 3.99 eV for singlet, triplet, quintet, septet and nonet states, respectively, matches with the calculated BEs of Goel et al. [29]. The calculated IP and EA values for Ni_4 cluster at singlet state are 5.30 eV (5.70 eV [40]) and 1.24 eV (1.50 ± 0.06 eV [41]), respectively, which well agrees with the experimental results inside the parentheses, and also previous theoretical study [30]. The singlet, quintet and nonet Ni_4 clusters are distorted tetrahedral geometry and shows zero dipole moment, whereas triplet and septet states are butterfly structure, produces greater dipole moment. The nonet Ni_4 cluster shows the highest hardness, 2.36 eV, indicating most stable state. Natural bond orbital analysis data shows, that the clusters are more stable due to change of nature of hybridization from '*sd*' to '*sp*' at higher multiplicity, as shown in Supplemental Table S6.

3.2. Adsorption and Dissociation of CO on Ni_4 Cluster

The stable adsorption geometry of CO on tetrahedral Ni_4 cluster at different multiplicity are presented on Fig. 3(a,b) (IS), and adsorbed at three fold site (c_3) in μ_3-C pattern on the clusters, except quintet state (μ_2-C) in PBE method. No stable adsorption geometry is observed for triplet and quintet state in PBE method, whereas in hybrid PBE1PBE method binding is possible for all singlet to nonet Ni_4 clusters. The calculated ΔG values are negative, indicating adsorption or binding of CO on Ni_4 cluster is thermodynamically feasible process at normal condition. The C—O bond distance is elongated to 1.218 Å,1.188 Å and 1.198 Å on singlet, quintet and septet, respectively due to the weakening of bond strength, and corresponding stretching frequencies are 1637.31 cm^{-1}, 1789.59 cm^{-1} and 1728.45 cm^{-1}, respectively. The calculated stretching frequency for isolated CO is 2126.30 cm^{-1} (in PBE method), exp. 2170 cm^{-1} [42]. Since CO is an electron-deficient molecule, the natural population analysis shows that charge transfer to cluster during adsorption are 0.37, 0.20, and 0.39 for singlet, quintet and



(a)PBE/LANL2DZ (b) PBE1PBE/LANL2MB

Fig. 1. Ground state geometries of higher spin Ni_4 clusters.

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