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Activity and selectivity of Ni nanoclusters in the selective hydrogenation of acetylene: A computational investigation

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ABSTRACT

In this work, the Ni_n ($n = 2-10$) nanoclusters were investigated to design new catalysts for the selective hydrogenation of acetylene. Our results show that among the Ni_n nanoclusters, the Ni₆ nanocluster can be used as a catalyst in the reactions of hydrogenation. In the presence of the Ni₆ nanocluster, the E_a of the forward step in the reaction of conversion of vinyl to ethylene was 21.21 kJ/mol lower than that of the reverse step in the reaction of conversion of acetylene to vinyl. Also, the E_a of the forward step in the reaction of conversion of ethyl to ethane was 96.59 kJ/mol higher than that of the reverse step in the reaction of conversion of ethylene to ethyl. According to the obtained results, the Ni₆ nanocluster can selectively act in the hydrogenation of a mixture of acetylene and ethylene.

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1. Introduction

One of the most interesting subjects for studying metal nanoclusters is to understand how their physical and chemical properties change as a function of size [1–15]. The size-selected metal nanoclusters are under investigation as the foundation for designing a new generation of catalysts [5,15–17]. By studying the properties of nanoclusters as a function of size, the researchers hope to provide better insight into factors governing transition-metal-centered chemistry. Also, it can provide important clues to the understanding of the mechanism of catalysis and other chemical properties [18,19]. More theoretical and experimental studies on the clusters improve the process of understanding their structures, electronic properties, and catalysis [1,4,5,7,11–14,17]. The geometry and electronic properties of nanoclusters have been successfully predicted by theoretical methods. In the literature, there are many

reports that investigate the properties of nanoclusters. Among these studies, nickel nanoclusters are the subject of many experimental and theoretical studies because these nanoclusters are very efficient catalysts for the hydrogenation and dehydrogenation of olefin reactions [11,20].

Ethylene is an important intermediate in the petrochemical industry. It is predominantly produced by the thermal or catalytic cracking of hydrocarbons [21]. The small amounts of coproduced acetylene in the ethylene stream can poison catalysts of ethylene polymerization [21]. The reaction of catalytic-selective hydrogenation is the preferred method to reduce the amount of acetylene because of its relative ease. In this reaction, at first, a hydrogen molecule is chemisorbed on a catalyst surface, and in the next step, this surface hydrogen reacts with acetylene. In fact, the dissociative adsorption of the hydrogen molecule is a necessary step for the hydrogenation of acetylene [21].

By the use of the theoretical studies we can specify some of the elementary reaction steps on catalyst surfaces and provide ideas about the reaction pathways. The density functional theory (DFT) calculations have been used to examine the adsorption modes for atomic hydrogen,

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acetylene, vinyl, and ethylene on different metal surfaces [7,10,13,14,17,22–24]. For instance, Chen and Vlachos [25] investigated the hydrogenation of ethylene and dehydrogenation of ethane on Pt(111) and Pt(211) using DFT method. The DFT calculation of selective hydrogenation reactions over Pd–Ag bimetallic catalysts was investigated by Gonzalez et al. [26]. Also, the thermodynamic properties of the acetylene and ethylene hydrogenation on some bimetallic Pd–Ag alloy catalytic surfaces were theoretically studied by Sheth et al. [27].

The present study aims at reporting the results of hydrogenation of acetylene and ethylene on nickel nanoclusters by DFT calculations. The first step in the hydrogenation is the dissociative adsorption of hydrogen molecule, and therefore, we initially studied the quality of the adsorbed hydrogen on the nickel nanoclusters. Then, the adsorption of acetylene, ethylene, along with the vinyl and ethyl intermediates is discussed. Furthermore, we investigate the activity and selectivity of these surfaces.

2. Methodology

All the geometry optimization of ground states and transition states (TSs) were carried out through a high quantum level of DFT-D (Dispersion-corrected Density Functional Theory) approach implemented in the DMol³ program package [28,29]. In this work, the PBE (Perdew, Burke and Ernzerhof) functional [30] with Grimme's long-range dispersion correction [31] (PBE-G) was used. We selected fine grid for the numerical integration of the exchange–correlation functions and related matrix elements. The effective core potentials (ECPs) and double-numerical quality basis function with polarization function for H atoms (DNP) were selected for all atoms. We considered the high spin multiplicity of the Ni nanoclusters to find the lowest energy spin state (1, 3, 5, and 7 for odd multiplicity systems and 2, 4, 6, and 8 for even multiplicity systems). The spin state with the lowest electronic energy was used for the computation of geometry and electronic properties. No symmetry constraints are imposed for obtaining the equilibrium geometries of the structures for each possible spin multiplicity. The stationary geometries were characterized as minima or TSs by analytical frequency calculations at the same level as the geometry optimizations. To determine the activation energy for a specific reaction pathway, a TS was identified by the complete linear synchronous transit and the quadratic synchronous transit methods. Also, the TS structure was confirmed by the nudged elastic band method using TS confirmation calculations.

The adsorption energy (E_{ads}) was calculated as follows:

$$E_{\text{ads}} = E_{\text{complex}} - \left(\sum E_{\text{fragment}} \right) \quad (1)$$

where E_{complex} is the total energy of the complex and E_{fragment} is the energy of different constituent parts of the complex. The reaction energy (E_{rxn}) was calculated as

$$E_{\text{rxn}} = \left(\sum E_{\text{products}} \right) - \left(\sum E_{\text{reactants}} \right) \quad (2)$$

3. Results and discussion

3.1. Acetylene and ethylene adsorption on the Ni_n (n = 2–10) nanoclusters

Acetylene adsorption: in our previous work [32], we investigated the geometric structures of Ni_n (n ≤ 10) nanoclusters in their lowest energy state. In this work, we used the most stable structure of the Ni_n (n = 2–10) nanoclusters as substrates and the adsorption energy of C₂H₂ on these nickel nanoclusters is calculated. All structures are optimized at the PBE-G/DNP-ECP level of theory. The optimized structure with the maximum adsorption energy is determined as the most stable structure. The most stable adsorption modes of C₂H₂ on the Ni_n (n = 2–10) nanoclusters, as well as the adsorption energies (E_{ads}) and corresponding multiplicities (2S + 1) are reported in Table 1.

According to Table 1, the C₂H₂ adsorption on these nickel nanoclusters is selective in π-coordination. This means that the two C atoms prefer to bond with the same Ni atom. In all structures, the C–H bonds are distorted out of the acetylene plane (Table 1). We can explain this condition by the electron donation and electron back donation between the hybridized orbital of the Ni_n nanoclusters and the hybridized orbital of the acetylene molecule. The results show a good overlap between these orbitals and the increase in interactions between the nickel nanoclusters and the acetylene molecule as well. The range of the adsorption energy for the C₂H₂ adsorption is –146.27 to –177.34 kJ/mol. From comparison of the Ni_n nanoclusters, it can be said that the acetylene adsorption on the Ni₅ and Ni₄ nanoclusters is more effective than other nickel nanoclusters.

Ethylene adsorption: to investigate the adsorption of ethylene on the Ni_n (n = 2–10) nanoclusters, different structures were designed and optimized at the PBE-G/DNP-ECP level of theory. The optimized structure with the maximum adsorption energy is determined as the most stable structure.

The most stable adsorption modes of C₂H₄ on the Ni_n (n = 2–10) nanoclusters, as well as the adsorption energies (E_{ads}) and corresponding multiplicities (2S + 1) are reported in Table 2. Accordingly, the C₂H₄ adsorption on these nickel nanoclusters is selective in π-coordination. The range of C₂H₄ adsorption energy is –126.23 to –153.89 kJ/mol. The ethylene adsorption on the Ni₅ and Ni₄ nanoclusters is more effective than other nickel nanoclusters.

One of the catalytic drawbacks for acetylene hydrogenation is that acetylene is more easily adsorbed on the surface than the hydrogen molecule, and therefore, the catalytic active sites are occupied. Therefore, a catalyst can be effective when the adsorption energy of a hydrogen molecule on its surface is higher than that of an acetylene or ethylene.

The behavior of a material in bulk and nanoscale is very different and in most cases, nanoscale materials are much more active than the bulk. In our previous work [32], we investigated the adsorption energy for hydrogen on the Ni_n (n = 2–10) nanoclusters.

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