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Graphene-supported Cu_{11} nanocluster as a candidate catalyst for the selective hydrogenation of acetylene: A density functional study

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ABSTRACT

In this paper, by the density functional theory (DFT) calculations we show that the copper nanocluster can be used as catalyst for the hydrogenation of acetylene and ethylene. Since the nature of dissociation of hydrogen molecule on the copper nanocluster is the governing step for the hydrogenation reaction, the adsorption and complete dissociation of H_2 on the Cu_{11} nanocluster is investigated at PBE-G/DNP-ECP level of theory. The results show that H_2 is adsorbed dissociatively on the Cu_{11} nanocluster. To examine the activity of copper nanocluster as a catalyst for the hydrogenation reaction, the hydrogenations of acetylene and ethylene are investigated on the free Cu_{11} nanocluster, due to its highest adsorption energies for hydrogen, acetylene and ethylene adsorptions. In the presence of the Cu_{11} nanocluster as a catalyst, acetylene and ethylene can be hydrogenated to ethylene and ethane, respectively. These reactions are exothermic with the total reaction energies of −247.61 and −174.01 kJ/mol for hydrogenation of acetylene and ethylene, respectively. One of the interesting features of this catalyst is that the energy of acetylene adsorption on $Cu_{11}2H$ complex is higher than the energy of ethylene adsorption. It seems that Cu_{11} nanocluster can be used as catalyst for the selective hydrogenation of acetylene. Also, we choose graphene as a support for copper nanocluster and the hydrogenation of acetylene and ethylene on graphene-supported Cu_{11} nanocluster are investigated. Based on our DFT calculations, we suggest graphene-supported Cu_{11} nanoclusters as candidates with good activity and selectivity for the acetylene hydrogenation reaction.

1. Introduction

Ethylene is an important intermediate in the petrochemical industry. It is predominantly produced by the thermal or catalytic cracking of hydrocarbons. The small amounts of co-produced acetylene in the ethylene stream can poison catalysts of ethylene polymerization [1]. Reaction and separation are two general approaches to reduce the acetylene in the ethylene stream. The reaction of catalytic-selective hydrogenation is the preferred method to reduce the amount of acetylene because of its relative ease [2,3]. 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 [4]. The palladium catalysts, which dissociatively adsorb the hydrogen molecule, are commonly used catalysts for the hydrogenation reactions [4]. However, these catalysts have several fundamental problems. Firstly, acetylene is more easily adsorbed on Pd than hydrogen. For this reason, hydrogenation of acetylene is performed in an excess of hydrogen. The second problem is the high price of these catalysts. Also, this catalyst does not show good selectivity. Many studies have been carried out to overcome these problems. For example, it was shown that the Pd (111) close-packed surface is more selective than the Pd open surfaces [5–7]. Accordingly, in order to modify the selectivity over Pd nanocatalysts, some of the active sites can be blocked with other metals, such as Au, Ag, and Cu, or by a metal oxide, such as Ga_2O_3, La_2O_3 and TiO_2 [5,8–14]. In addition, some inert materials, including porous silica or carbonaceous deposits, have been used to achieve this goal [15,16]. Another approach for high selectivity in the hydrogenation of acetylene is to form supported single atom catalysts (SACs) by isolating Pd active sites with solid supports [7,17–19]. These SACs have shown good selectivity and activity in several catalytic processes. Sykes et al.

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substituted a single Pd atom into Cu (111) surfaces in order to use copper as a catalyst. They showed that these single Pd atoms were able to dissociatively adsorb the hydrogen molecule [20,21]. Also, study on the relationship between the catalytic performance of metal materials and their morphology was considered by many researchers [22–24]. The morphology and size of the particles can affect the performance of catalysts.

On the other hand, other catalysts have been considered for the selective hydrogenation of acetylene [7,25–27]. Some researchers showed that Au catalysts can have high selectivity for hydrogenation of acetylene [27,28]. The adsorption and hydrogenation of acetylene on Cu (110) and Cu (110)-O surfaces have been studied by Outka and co-workers [29]. Their result showed that acetylene was completely hydrogenated to ethylene on Cu (110)-O in the presence of excess surface hydrogen at 380 K.

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 calculations have been used to examine the adsorption modes for atomic hydrogen, acetylene, vinyl, ethylene on different metal surfaces [28,30–38]. For instance, Chen and co-workers investigated the hydrogenation of ethylene and dehydrogenation of ethane on Pt(111) and Pt(211) using DFT method [39]. The DFT calculation of selective hydrogenation reactions over Pd-Ag bimetallic catalysts was investigated by Neyman et al. [40]. 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. [36].

This work aims at reporting the results of hydrogenation of acetylene and ethylene on free and graphene-supported copper nanocluster by density functional theory calculations. The first step in the hydrogenation is the dissociative adsorption of hydrogen molecule, and therefore, we initially study the quality of adsorbed hydrogen on free and graphene-supported Cu_{11} nanocluster. Then, the adsorption of acetylene, ethylene, along with the vinyl and ethyl intermediates will be 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 approach implemented in the DMol^3 program package [41,42]. In this work, the PBE functional [43] with Grimme's long-range dispersion correction [44] (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. The stationary geometries were characterized as minima or transition states by analytical frequency calculations at the same level as the geometry optimizations. To determine the activation energy for a specific reaction pathway, a transition state was identified by the complete linear synchronous transit (LST) and the quadratic synchronous transit (QST) methods. Also, the TS structure was confirmed by the nudged elastic band (NEB) method using TS confirmation calculations.

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

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

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:

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

3. Results and discussion

Here, we consider Horuiti-Polanyi mode [4] of the reaction. In this mode, the C_2H_2 (or C_2H_4) is adsorbed on the surface and two sequential hydrogen addition steps take place from a reservoir of adsorbed hydrogen atoms. This mode is suitable to investigate the reactivity of the dissociatively adsorbed hydrogens on a surface. This is supported by the experimental evidences showing that complete dissociation of adsorbed H_2 is needed for the hydrogenation of acetylene on a catalyst surface [4]. Firstly, we try to explore the complete dissociation of adsorbed H_2 on copper nanocluster surface as shown in equation (3).

$$Cu_n + H_2 \rightarrow Cu_n2H \quad (3)$$

where Cu_n2H is the dissociatively adsorbed H_2 on the surface of Cu_n nanocluster.

Kuang et al. [9] found that H_2 was adsorbed dissociatively on the Cu_n (n = 10–13) nanoclusters, whereas a molecularly adsorption was seen for the Cu_n (n = 2–9) nanoclusters. Also, they found that the adsorption energy of H_2 on Cu_{11} was greater than other copper nanoclusters. So, we can use this nanocluster as catalyst for the hydrogenation of acetylene and ethylene. In our previous works [33,34], we investigated the geometric structures of Cu_n ($n \leq 15$) nanoclusters in their lowest energy state. Also, we investigated the adsorption energy for acetylene and ethylene on Cu_n (n = 10–15) nanoclusters. We showed that the values of adsorption energy for acetylene and ethylene adsorption on Cu_{11} nanocluster is greater than the other nanocluster. Therefore, in what follows, we use this nanocluster as a catalyst for the hydrogenation of acetylene and ethylene.

3.1. *Adsorption of H_2 on Cu_{11} nanoclusters*

In this work, we use the most stable structure of Cu_{11} nanocluster (Fig. 1a) as substrate and the adsorption energy of H_2 on this copper nanocluster is calculated. Fig. 1b shows the charge distribution over the Cu_{11} nanocluster, visualized via the electrostatic potential surface (ESP) map. This visualization can be used for finding the reactive sites of the molecules. For the visualization of ESP, the optimized structures at the level of PBE-D/DNP using DMol^3 code were employed by an equivalent method, i.e., PBEPBE/6-31G**, available in the Gaussian package. The maps were generated with isosurfaces of 0.01 electrons/au^3 through GaussView package, and the ESP analysis was undertaken by Multiwfn 2.4 program using the wavefunctions generated at PBEPBE/6-31G**. The relative abundance and absence of electrons are respectively related to the sites with the lowest (red region) and highest (blue region) values of electrostatic potential energy. The maximum ESP values on the local surface of Cu_{11} nanocluster are 98.7, 98.7, 43.08 and 42.75 kJ/mol, respectively (Fig. 1b). This result clearly explains the site-selectivity; the site with the value of 98.7 kJ/mol is the most favorable site because the ESP on its local surface is the most positive, and hence nucleophilic reagents tend to be attracted to this site.

To examine the reactivity indices of the copper atoms, their Fukui function *f(r)* are calculated. The Fukui function *f(r)* defined in the framework of density functional theory can be represented as: