Kinetic Study of Few Layer Graphene Growth on Cu-Ni Alloy Catalyst: A Density Functional Theory Approach

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ABSTRACT

The tunable electronic and optical properties of few layer graphene (FLG) make it transparent potential for conductive electrode applications. The FLG with precisely controlled number of layers can be grown using Chemical Vapor Deposition (CVD) method on the Cu-Ni alloy catalyst. effect However. the of Ni atom concentration in the Cu-Ni alloy catalyst on the FLG growth mechanism is still not fully understood. The kinetic aspect studies still be conducted need to to get а comprehensive picture of the growth process. Therefore, in this study, we use the density functional theory method to study the effect of Ni atom concentration on the growth mechanism of graphene on Cu-Ni alloy catalyst from the kinetic aspect. We consider two catalyst models, namely Cu-Ni-1 (6.25 at % Ni) and Cu-Ni-3 (18.75 at % Ni) catalysts and two kinetic processes, namely diffusion of C atoms over the catalyst surface and diffusion of C atoms from the surface to the subsurface of the catalyst. We found that increasing the concentration of Ni atoms causes a reduction in the activation energy of the diffusion of C atoms from the surface to the subsurface of the catalyst, which in the case of Cu-Ni-2 catalyst is 0.16 eV. This activation energy is lower than the single

atom energy at the graphene growth temperature (0.17 eV). This result indicates that Cu-Ni catalysts with Ni atom concentrations greater than 18.75% can be used to grow FLG with precisely controlled number of layers. This finding can be used as a guidance for experimental research in order to grow few layer graphene with high quality.

Keywords: density functional theory, electronic conductivity, few-layer graphene, transmittance

INTRODUCTION

Research on synthesizing graphene with a controlled number of layers has become a significant interest in advanced materials, especially for electronics, sensors, and optical device applications (1,2). One of the widely used methods for growing graphene is Chemical Vapor Deposition (CVD), which enables the production of highquality graphene on a large scale. However, the main challenge in this method is to control the number of graphene layers formed because factors such as the type of catalyst. temperature, and pressure significantly affect the nucleation and growth rates (3-5).Therefore, а fundamental understanding of the reaction kinetics mechanisms during the graphene growth process is required.

In order to overcome these challenges, the use of metal alloy-based catalysts, such as Cu-Ni, has attracted attention due to its ability to control the solubility of carbon atoms and the growth rate of graphene (6,7). The Cu-Ni alloy catalyst offers advantages compared to pure catalysts because they can balance the solubility and diffusivity of carbon atoms in the metal, which affects the formation of a few-layer graphene (8-10). However, the reaction mechanisms in the Cu-Ni catalyst, including surface and subsurface diffusion, are still not fully theoretical understood. Therefore. approaches, such as Density Functional Theory (DFT), can be used to investigate the underlying kinetic mechanisms of fewlayer graphene growth reactions.

DFT has become a reliable method for explaining chemical reaction phenomena on metal surfaces, including in heterogeneous catalysis processes such graphene as synthesis (11-13).This method can thermodynamic calculate and kinetic parameters such as adsorption energy, activation energy, and the most likely reaction pathways during the graphene growth process (14,15). DFT studies also allow exploration of the effects of Cu-Ni alloy composition on the reaction kinetics of the carbon atom diffusion process, which can ultimately help in designing more optimal catalyst conditions to control the number of graphene layers.

Therefore, this study uses the DFT method to elucidate the few-layer graphene growth reaction kinetics on a Cu-Ni catalyst with varying Ni atom concentrations. The results are expected to provide in-depth insight into the role of catalyst composition in controlling the number of graphene layers and help optimize growth parameters in the CVD method.

COMPUTATIONAL METHODOLOGY

This study will review two catalyst models: the Cu-Ni-1 catalyst (Ni atomic concentration of 6.25 at. %) and Cu-Ni-3 (Ni atomic concentration of 18.75 at. %). The Cu (111) crystal surface is chosen as the basic model. This selection is based on the fact that the Cu (111) catalyst has a lattice constant that resembles graphene, resulting in a low lattice mismatch (8). The Cu (111) catalyst is modeled with four (2×2) supercell layers and a vacuum layer of 15 Å height along the z-axis direction to avoid interactions between adjacent cells. The Cu-Ni-1 alloy catalyst is modeled by substituting one Cu atom on the top layer of the Cu (111) system with one Ni atom. To model the Cu-Ni-3 catalyst, three Cu atoms in the first to third layers of the Cu (111) system are substituted with three Ni atoms. The crystal structure of the Cu-Ni alloy catalyst model with various Ni atomic concentrations is shown in Figure 1.



Figure 1. The crystal structures of Cu, Cu-Ni-1, and Cu-Ni-3 alloy catalyst models.

The climbing image-nudged elastic band (CI-NEB) method based on density functional theory (DFT) was used to evaluate the diffusion kinetics of the C monomer. The CI-NEB method has been implemented in the Quantum ESPRESSO

code (16,17). The projected augmented (PAW) method regulated wave the interaction of valence electrons with the ion core (18). The Perdew–Burke–Ernzerhof (PBE)-based generalized gradient approximation (GGA) functional was used to approximate the exchange-correlation interaction (19). In the CI-NEB method, the configurations initial and final are six intermediate connected with state configurations to be optimized until the minimum energy path (MEP) is achieved. The optimization process is carried out until the force is no more than 0.02 eV/Å. The wave function is expanded with a plane wave basis with the cut-off energy set at 816 eV. Gaussian smearing with a broadness of 0.01 eV was used to determine the electron occupancy. The weak van der Waals interactions were also considered by implementing the semi-empirical DFT-D2 approach.

RESULT AND DISCUSSION

Kinetics is a crucial aspect that needs to be reviewed in addition to energetics and thermodynamics to see the possible chemical processes in graphene growth. Diffusion of C monomers plays an important role in controlling the graphene growth mechanism. In this study, we want to check the kinetics of possible diffusion pathways of C monomers, including surface diffusion and diffusion from the surface to the sub-surface. From the kinetic analysis, MEP can be found, then the activation energy (E_A) and product energy (E_P) can be determined by the following equations:

$$E_A = E_{TS} - E_{IS} \quad (1)$$
$$E_P = E_{FS} - E_{IS} \quad (2)$$

Where E_{IS} , E_{TS} , and E_{FS} are the energies at the initial, transition, and final states, respectively.



Figure 2. Energy profiles of C monomer diffusion on the surface of Cu, Cu–Ni-1, and Cu–Ni-3 catalysts. IS, TS, and FS indicate the initial, transition, and final states, respectively.

Kinetic analysis was conducted to validate the transformation of active species of carbon source from C monomer on the catalyst surface to C monomer on the catalyst sub-surface. Figures 2 (a)-(c) show the energy profile of the C monomer diffusion on the surface of Cu, Cu-Ni-1, and Cu-Ni-3 catalysts, respectively, where the structures of the initial and final state are C monomer placed on the sites related to the second and first lowest adsorption energies. The addition of Ni atoms does not significantly affect the surface diffusion process of C monomers, which only observed a slight decrease in activation energy after alloying Ni atoms. The increase in the fraction of Ni atoms also does not significantly affect the energy profile of the C monomer surface diffusion. This condition is predicted because the surface

diffusion process of C monomers is only influenced by Cu or Ni atoms on the surface, which, in this study, the Cu-Ni-1 and Cu-Ni-3 catalysts are modeled with the same density of Ni atoms on the catalyst surface.

Figures 3(a)-(c) show the energy profiles of the diffusion of C monomers from the surface to the subsurface of Cu, Cu-Ni-1, and Cu-Ni-3 catalysts, respectively, which the structures of the initial and final state are C monomers placed on the surface and subsurface sites corresponding to the lowest adsorption energy, respectively. It has been observed that the alloying of Ni causes a significant decrease in the product energy. This condition causes diffusion to the which initially subsurface. was an endothermic process in pure Cu catalysts, to become an exothermic process in Cu-Ni catalysts. Increasing the fraction of Ni atoms further decreases the product energy, which, in Cu-Ni-3 catalyst, the product energy becomes -0.59 eV.



Figure 3. Energy profiles of C monomer diffusion from surface to the sub-surface of Cu, Cu–Ni-1, and Cu–Ni-3 catalysts. IS, TS, and FS indicate the initial, transition, and final states, respectively.

Moreover, the addition of Ni atoms can also reduce the activation energy of the C monomer diffusion from the surface to the sub-surface of the catalyst. In the Cu-Ni-1 catalyst, the activation energy is reduced to 0.59 eV. However, even though the activation energy has been reduced, the activation energy is still relatively high compared to the average energy of a single atom at a temperature of 1300 K, which is 0.17 eV. Thus, the diffusion of C monomers to the sub-surface of the Cu-Ni-1 catalyst is not kinetically favored. This indicates that the growth mechanism of graphene on the Cu-Ni alloy catalyst with a low Ni concentration will be the same as the growth mechanism on the pure Cu catalyst. Further increasing the fraction of Ni atoms can reduce the activation energy, which in the Cu-Ni-3 catalyst is 0.16 eV. This activation energy is lower than the energy of a single atom at the growth temperature. Therefore, only a Cu-Ni-3 catalyst (Ni atomic fraction is \sim 18.75%) can facilitate the diffusion process of C atoms into the sub-surface of the catalyst. This result shows that a Cu-Ni catalyst with a Ni atomic fraction of more than 18.75% has the potential to be used to grow FLG with a precisely controlled number of layers.

CONCLUSION

We have studied the kinetics of C monomer diffusion on Cu-Ni alloy catalysts with various Ni atomic concentrations using the method. The variations of Ni DFT concentrations were 6.25% (Cu-Ni-1) and 18.75% (Cu-Ni-3). Alloying with Ni atom did not significantly affect the diffusion of monomer on the catalyst surface. С significantly However, it reduced the activation and product energy of С

monomer diffusion from the surface to the sub-surface. Furthermore, an increase in Ni concentration made the diffusion process of C monomers from the surface to the subsurface more exothermic. Moreover, only a Cu-Ni-3 catalyst with a Ni fraction of 18.75% effectively facilitated the diffusion of C monomers to the sub-surface. This condition indicates a change in the active species of the carbon source from C monomers on the catalyst surface to C monomers on the catalyst sub-surface. Therefore, only Cu-Ni catalysts with Ni fractions greater than 18.75% can potentially grow FLG with a controlled layer number.

Declaration by Authors

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REFERENCES

- 1. Yazıcı Hİ, Schulz C, Daun KJ. Feasibility of online optical diagnostics during gas-phase synthesis of few-layer graphene based on elastic light scattering measurements. Journal of Aerosol Science. 2025; 184:106497.
- Flores-Arciniega JL, Acosta S, Ojeda-Galván HJ, López-Sánchez V, Sánchez-Balderas G, Yáñez-Soto B, et al. Design of graphene oxide/few layers graphene 2D heterostructured membranes (GO/FLG-m) for water purification. Carbon. 2025; 234:119924.
- Behera S. Nonlinear electronic devices on single-layer CVD graphene for thermistors. Nanotechnology. 2024;35(50):505710.
- Yang Y, Yuan H, Liu M, Cheng S, Li W, Liang F, et al. Premelted-Substrate-Promoted Selective Etching Strategy Realizing CVD Growth of High-Quality Graphene on Dielectric Substrates. ACS Applied Materials & Interfaces. 2025;17(4):6825–34.
- Behera S. Pure edge-contact devices on single-layer-CVD-graphene integrated into a single chip. Scientific Reports. 2023;13(1):10588.
- 6. Zhou Z, Ng YH, Xu S, Yang S, Gao Q, Cai X, et al. A CuNi Alloy–Carbon Layer Core–

Shell Catalyst for Highly Efficient Conversion of Aqueous Formaldehyde to Hydrogen at Room Temperature. ACS Applied Materials & Interfaces. 2021;13(31):37299–307.

- Papon R, Sharma KP, Mahayavanshi RD, Sharma S, Vishwakarma R, Rosmi MS, et al. CuNi binary alloy catalyst for growth of nitrogen-doped graphene by low pressure chemical vapor deposition. Physica Status Solidi. 2016;10(10):749–52.
- Arya C, De Silva KKH, Yoshimura M. Adlayer-free large-area single-crystal CVD graphene growth on copper. Journal of Materials Science: Materials in Electronics. 2020;31(24):21821–31.
- Bekdüz B, Kaya U, Langer M, Mertin W, Bacher G. Direct growth of graphene on Ge(100) and Ge (110) via thermal and plasma enhanced CVD. Scientific Reports. 2020;10(1):12938.
- Li N, Zhang RJ, Zhen Z, Xu ZH, Mu RD, He LM. The effect of catalytic copper pretreatments on CVD graphene growth at different stages. Nanotechnology. 2020;32(9):095607.
- Zhou W, Li Z, Li L, Zeng W, Zhou Q. Adsorption and detection of SF6 decomposed toxic gases (H2S, SO2, SOF2, SO2F2) on transition metal (Fe, Ru, Os) modified WTe2 monolayer: A DFT investigation. Journal of Environmental Chemical Engineering. 2025;13(2):115545.
- Hessen AS, Ahmed Alsultany NM, Bahir H, Adthab AH, Soleimani-Amiri S, Ahmadi S, et al. Adsorption of sulfur mustard on the transition metals (TM = Ti2+, Cr2+, Fe2+, Co2+, Ni2+, Cu2+, Zn2+) porphyrins induced in carbon nanocone (TM-PCNC): Insight from DFT calculation. Journal of Molecular Graphics and Modelling. 2025; 135:108928.
- 13. Khosrowshahi MS, Hariri SA, Rahimi M, Emrooz HBM, Shemirani F. Green synthesis of a ZnO/ZnS-decorated magnetic porous carbon hybrid for enhanced rhodamine B adsorption and photodegradation: A combined DFT and experimental study. Sustainable Materials and Technologies. 2025;43: e01231.
- 14. Fernandes FM, Xavier NF, Bauerfeldt GF, Pereira MS, da Silva CO. Thermodynamic and kinetic analysis of the oxygen evolution reaction on TiO2 (100) and (101) surfaces:

A DFT study. Surface Science. 2025; 753:122654.

- 15. Liu L, Li K, Liu H, Sun Z. A DFT-based kinetic equation for Co3O4 decomposition reaction in high-temperature thermochemical energy storage. Applied Thermal Engineering. 2025; 260:125064.
- 16. Giannozzi P, Andreussi O, Brumme T, Bunau O, Nardelli MB, Calandra M, et al. Advanced capabilities for materials modelling with Quantum ESPRESSO. Journal of Physics: Condensed Matter. 2017;29(46):465901.
- 17. Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of

materials. Journal of Physics: Condensed Matter. 2009;21(39):395502.

- Blöchl PE. Projector augmented-wave method. Physical Review B. 1994; 50(24):17953–79.
- Perdew JP, Burke K, Ernzerhof M. Generalized Gradient Approximation Made Simple. Physical Review Letter. 1996; 77(18):3865–8.

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