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First Principles Investigation of Adsorption Mechanisms and Charge Redistribution for CH_4/Ni(111) Surface

دراسة من المبادئ الأولى لآلية الامتزاز وإعادة توزيع الشحنة لجزيء الميثان (CH_4) على سطح النيكل Ni(111)

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Abstract: Liquefied natural gas (LNG) is predominantly methane (CH_4), and the characterization of its interaction to metallic materials (e.g., nickel) is important for evaluating structural stability during cryogenic storage and transport. Using density functional theory within the GGA–PBE framework as implemented in QuantumATK 2023, the adsorption behavior of a single CH_4 molecule on a six-layer Ni(111) surface was evaluated in this work. The surface was simulated using a 4×4 slab configuration with a vacuum layer sufficiently large to prevent interactions between periodic images. The upper three Ni layers and methane molecule were completely relaxed during the optimization. The optimized structure shows that methane maintains its ideal tetrahedral geometry (C–H ≈ 1.11 Å) but the equilibrium C–Ni separation is approximately 3.21 Å, while Ni–Ni interlayer distances do not change significantly, indicating a minimal structural distortion of the metallic slab. The calculated adsorption energy (E_{ads} = −1.22 eV) indicates energetically favorable adsorption of methane on the Ni(111) surface, suggesting a relatively weak interaction characteristic of physisorption. Density of states (DOS) analysis further confirms that the electronic states near the Fermi level are dominated by Ni 3d orbitals, while methane-related states contribute only weakly, indicating negligible orbital hybridization and confirming the physisorption nature of CH_4 adsorption on the Ni(111) surface. Bader charge analysis further reveals negligible net charge transfer and minimal interfacial polarization. Electron density difference (EED) analysis reveals only minor charge redistribution at the CH_4/Ni(111) interface, indicating negligible charge transfer and supporting the weak physisorption nature of methane adsorption on the Ni(111) surface. In general, we find that the methane interaction with Ni(111), governed primarily by weak van der Waals forces, is relatively weak and no covalent bond or activation occurs. These results confirm the electronic and chemical inertness of methane on clean nickel surfaces under cryogenic conditions relevant to LNG storage and transport systems.

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الملخص: الغاز الطبيعي المُسال (LNG) يتكوّن في معظمه من الميثان(CH_4) ، وتُعد دراسة طبيعة ارتباطه بالمواد المعدنية المسمثل النيكل (أمرًا مهمًا لتقييم الاستقرار البنيوي أثناء عمليات التخزين والنقل في الظروف الكريوجينية . في هذا العمل تم استخدام نظرية الكثافة الوظيفية (DFT) ضمن إطار GGA–PBE كما هو مُطبَّق في برنامج QuantumATK 2023لدراسة سلوك امتزاز جزيء واحد من الميثان على سطح Ni(111) المكوَّن من ست طبقات .وقد تم تمثيل السطح باستخدام نموذج slab بحجم 4×4 مع طبقة فراغ كبيرة بما يكفي لمنع التفاعل بين الصور الدورية للنظام.

خلال عملية التحسين الهندسي، سُمِح للطبقات الثلاث العلوية من النيكل وكذلك جزيء الميثان بالاسترخاء الكامل . تُظهر البنية المحسَّنة أن جزيء الميثان يحافظ على شكله رباعي السطوح المثالي(C–H≈1.11 A°) ، بينما يبلغ البعد المتوازن بين الكربون والنيكل حوالي .3.21 A° كما أن المسافات البينية بين طبقات النيكل (Ni–Ni) لا تتغير بشكل ملحوظ، مما يشير إلى حدوث تشوّه بنيوي طفيف جدًا في السطح المعدني.

تشير طاقة الامتزاز المحسوبة (Eads=−1.22 eV) إلى أن امتزاز الميثان على سطح Ni(111) مفضل طاقيًا، إلا أن قوة التفاعل ضعيفة نسبيًا، وهو ما يميّز الامتزاز الفيزيائي .كما يؤكد تحليل كثافة الحالات الإلكترونية أن الحالات الإلكترونية القريبة من مستوى فيرمي يهيمن عليها أساسًا مدار Ni 3d ، في حين أن مساهمة الحالات المرتبطة بالميثان ضعيفة جدًا، مما يدل على غياب تهجين مداري ملحوظ ويؤكد الطبيعة الفيزيائية لامتزاز CH4 على سطح النيكل.

كذلك يُظهر تحليل Bader للشحنة عدم وجود انتقال صافٍ للشحنة تقريبًا مع استقطاب طفيف جدًا عند الواجهة . ويكشف تحليل فرق الكثافة الإلكترونية عن إعادة توزيع محدودة للشحنة عند واجهة(CH4/Ni(111 ، مما يشير إلى انتقال شحنة ضئيل ويدعم الطبيعة الفيزيائية الضعيفة لامتزاز الميثان على هذا السطح.

بصورة عامة، تُظهر النتائج أن تفاعل الميثان مع سطح Ni(111) تحكمه أساسًا قوى فان دير فال الضعيفة، وبالتالي فإن هذا التفاعل ليس قويًا بما يكفي لتكوين رابطة تساهمية أو لتنشيط جزيء الميثان .وتؤكد هذه النتائج الخمول الإلكتروني والكيميائي للميثان على أسطح النيكل النظيفة في الظروف الكريوجينية المرتبطة بتقنياتLNG

الكلمات المفتاحية: نظرية دالة الكثافة(DFT) ، الامتزاز، السطح، إعادة توزيع الشحنة، الغاز الطبيعي المُسال (LNG)

1. INTRODUCTION

Liquefied natural gas (LNG) has become one of the fastest growing energy carriers globally due to its high energy density, accessibility for long-distance transport and relatively low greenhouse gas emission rates compared with conventional fossil fuels (BP, 2023; Mokhatab et al., 2014; Wang et al., 2025). Methane (CH_4) constitutes more than 90 % of LNG, which makes its physicochemical stability within cryogenic (≈110–140 K) and high-pressure conditions, as a technical necessity. Knowledge of methane's interaction with structural metallic materials used in transport, storage, and regasification within LNG infrastructure is essential to ensure safe storage, transfer, and regasification (Gao et al., 2022; Zonfrilli et al., 2023). Methane is typically present as a weakly interacting molecular species under cryogenic conditions. Even though CH_4 is chemically inert, slight interactions between it and metallic surfaces can affect adsorption performance and interfacial charge distribution. Thus, the

atomic scale evaluation of methane–metal interfaces is crucial for assessing of LNG material compatibility and operational reliability. Many cryogenic engineering systems and catalytic methane conversion technologies use nickel-bearing materials. Ni-containing alloys in LNG processing have been extensively used mainly in pipelines, storage and heat-exchangers, owing to their mechanical resistance and low-temperature corrosion resistance at LNG plants (Gao et al., 2022; Mokhatab et al., 2014; BP, 2023; Wang et al., 2025). From the viewpoint of surface science, the Ni(111) facet is one of the most thermodynamically stable and extensively studied nickel surfaces, which makes it an appropriate model for studying methane–metal interactions. Although several studies have investigated methane activation and C–H bond dissociation on Ni surfaces at elevated temperatures (Bligaard et al., 2004; Sehested et al., 2004; Wang & Wang, 2024; Zhai et al., 2021), there have been comparatively few studies focused on the weak adsorption phenomena under LNG storage conditions. Methane adsorption was also extensively investigated in low dimensions materials by first principle processes. For example, Ren et al. (2019) investigated CH_4 adsorption on MoX_2 (X = S, Se, Te) monolayers and found that this interaction is mainly mediated through weak van der Waals forces with minimal charge redistribution in the substrate. Similarly, Zhang et al. (2017) demonstrated through DFT calculations that m{ethane adsorption on graphene is dominated by physisorption with very low adsorption energies. Boukhvalov & Katsnelson (2008) presented a wider theoretical perspective of interactions between hydrocarbons and graphene, pointing out that significant charge transfer does not occur during methane adsorption except at defect or catalytic sites. Consistent with such results, Koh et al. (2012) investigated the adsorption and diffusion of CH_4 on MoS_2 monolayers, confirming that methane is relatively weakly bound, and has a minimal electronic effect on the host surface. Apart from 2D materials, Ren et al. (2021) thoroughly analyzed the activation of methane on metallic systems and emphasized that the significant charge transfer and bonding dissociation happens mainly under the conditions of high temperature and reactivity. At low temperatures, methane generally retains its molecular structure and reacts relatively weakly with clean metal surfaces. On the methodology front, DFT offers a comprehensive framework for studies of adsorption energetics and interfacial charge redistribution at the atomic scale. The theoretical basis of DFT is described in detail by (Martin, 2004) and total-energy approaches were systematically proposed by (Neugebauer & Scheffler ,1992) for analysis of adsorbate-substrate interactions. Such computational approaches allow for the faithful determination of adsorption energies and to run the charge transfer analysis that is required to explain weakly interacting systems like methane-to-metal. Much previous density functional theory (DFT) attention has focused on methane decomposition pathway, catalytic interaction barriers, and high-temperature chemisorption mechanisms. The initial adsorption property and the possibility of charge transfer from CH_4 to clean Ni surfaces have been uncertain under cryogenic conditions for several years. Even for weak physisorption, modest interfacial charge rearrangements can offer important evidence on the inertness and surface stability of methane. Despite several theoretical studies on methane activation on metal surfaces, the adsorption behavior and electronic interaction of methane on clean Ni(111) surfaces under conditions relevant to LNG storage systems remain insufficiently understood.

In this context, the current work aims to systematically analyze the adsorption of one CH_4 molecule onto the surface of Ni(111) using first-principles calculations. Particular focus is placed on evaluating

the adsorption energy and Bader charge to measure the potential charge transfer of methane to the nickel substrate. The goal of this study is to assess whether methane has any detectable electronic interactions with Ni(111) at low temperature, through the analysis of optimized geometries and interfacial charge redistribution. By focusing on a first-principles investigation, an atomic knowledge of methane–nickel interactions is obtained, which is directly applicable to LNG storage systems. The results of this analysis can provide fundamental insights into methane stability on metallic surfaces and can assist the development of safe and robust LNG.

In addition to fundamental surface science interest, understanding methane–metal interactions is also important for modern energy technologies. In particular, the stability of methane molecules on metallic surfaces plays a crucial role in liquefied natural gas (LNG) storage and transportation infrastructure. Atomic-scale investigations of methane adsorption on metallic systems therefore contribute to the development of safer cryogenic storage materials and improved LNG handling technologies. In this context, first-principles calculations provide a powerful tool for evaluating adsorption energetics and charge redistribution mechanisms at the methane–metal interface.

Therefore, the present work aims to provide a systematic first-principles investigation of methane adsorption on the Ni(111) surface. Particular attention is devoted to adsorption energetics, optimized adsorption geometry, and interfacial charge redistribution using Bader charge analysis. Such atomic-scale insights are important for evaluating the interaction strength between methane molecules and nickel-based materials used in LNG storage and transportation systems.

The present study provides a comprehensive first-principles investigation of methane adsorption on the Ni(111) surface by combining adsorption energy analysis with electronic structure characterization using DOS, Bader charge, and electron density difference (EED) calculations. Such a combined analysis offers deeper insight into the adsorption mechanism and electronic interaction between methane and metallic surfaces relevant to LNG storage systems. Therefore, the main objective of this study is to investigate the adsorption mechanism of methane on the Ni(111) surface using first-principles density functional theory calculations. Particular attention is given to the adsorption energy, electronic structure, charge redistribution, and interaction mechanism between the methane molecule and the nickel surface.

Despite extensive studies on methane activation and catalytic decomposition on nickel surfaces at elevated temperatures, relatively few studies have focused on the weak adsorption behavior of methane on clean Ni(111) surfaces under cryogenic conditions relevant to LNG storage systems.

2. LITERATURE REVIEW

Methane interaction with metallic surfaces is extensively studied owing to its importance in the fields of catalysis, surface chemistry, and energy applications. Nickel surfaces, with Ni(111) being a prominent example, have been investigated as active catalysts in both methane reforming and catalytic activation processes. Methane is chemically stable and interacts weakly with clean metal surfaces under low

temperatures in both experimental and theoretical studies. Various studies have used DFT calculations to investigate methane adsorption on transition-metal surfaces. Arevalo et al. (2017) reported that methane adsorption on Ni(111) is marked by small adsorption energies that indicate weak physisorption but minimal bonding interaction.

Several previous studies have investigated methane adsorption and activation on nickel-based catalytic systems. For instance, Arevalo et al. (2017) reported that methane adsorption on Ni(111) surfaces is characterized by weak interaction energies prior to C–H bond activation. Similarly, Ren et al. (2021) discussed the fundamental principles governing methane activation on metal surfaces, emphasizing that methane activation typically requires elevated temperatures. Furthermore, Zhai et al. (2021) and Yan et al. (2025) demonstrated that methane adsorption on Ni-based catalytic systems generally occurs through weak physisorption before the onset of catalytic activation. These findings indicate that methane typically remains in a non-reactive molecular state on close-packed Ni surfaces and provide an important theoretical background for understanding methane–metal surface interactions.

In addition to the metallic systems, methane adsorption has been investigated in other two-dimensional materials too. Ren et al. (2019) studied CH_4 adsorption on MoX_2 monolayers demonstrated weak van der Waals interactions with minimal charge redistribution. Zhang et al. (2017) reported similar results for methane adsorption on grapheme, confirming that the adsorption process is driven by dispersion forces. The results of Boukhvalov & Katsnelson (2008) also supported that methane functionalization of graphene surfaces leads to negligible charge transfer in the absence of defects. However, few studies are available on methane–metal interactions under cryogenic conditions for storage and transportation of liquefied natural gas (LNG). Understanding the adsorption properties and the potential charge redistribution along the methane–nickel interface is thus important to evaluate the stability of LNG infrastructure materials. In this regard, a full first-principles investigation of methane adsorption on the Ni(111) surface is performed in this work, with particular focus on the adsorption energetics and interfacial charge transfer.

3. THEORETICAL BACKGROUND

Density functional theory (DFT) (Hohenberg & Kohn, 1964) is a computational technique extensively used to evaluate atomic-scale electronic structure and adsorption properties of materials. The total energy of atoms, molecules, and solids can predict their structural and electronic behaviors accurately since, in DFT, the overall energy of any system can be described as a functional of the electron density. The adsorption energy is one of the key parameters in adsorption studies to determine the interaction strength between a solid surface and an adsorbate molecule. The adsorption energy is calculated from the following relation:

$$E_{ads} = E_{Ni(111)} + E_{CH_4} - E_{Ni+CH_4} \quad (1)$$

Aside from adsorption energy analysis, charge redistribution at the interface between the molecule and the surface can be helpful in determining whether the interaction involves electron charge transfer.

Bader charge analysis is widely employed to study charge transfer between atoms in a system, as well as determine where electron charge accumulation or depletion occurs during adsorption.
Charge transfer between methane and the Ni(111) surface was analyzed using the Bader charge analysis method (Henkelman et al., 2006).

In order to obtain deeper insight into the electronic interaction between the methane molecule and the Ni(111) surface, the electron density difference (EED) analysis was performed. The electron density difference is calculated as:

$$\Delta\rho = \rho(CH_4 / Ni(111)) - \rho(Ni(111)) - \rho(CH_4) \quad (2)$$

Where (CH_4/Ni(111)) represents the total electron density of the adsorption system, while ρ(Ni(111)) and ρ(CH_4) correspond to the electron densities of the isolated Ni(111) surface and the methane molecule, respectively. These theoretical approaches enable an extensive exploration of adsorption and the electronic interaction between methane molecules and metallic surfaces.

4. METHODOLOGY

First-principles calculations were performed within the framework of Density Functional Theory (DFT) using the QuantumATK 2023 simulation package. The exchange–correlation interactions were described using the generalized gradient approximation (GGA) parameterized by Perdew–Burke–Ernzerhof (PBE) (Perdew et al., 1996). To properly account for weak dispersion interactions between methane and the nickel surface, Grimme's D3 dispersion correction was included. The Ni(111) surface was modeled using a six-layer slab consisting of 54 atoms within a 4×4 surface supercell. The relatively large supercell helps reduce interactions between periodic images of the adsorbate and ensures reliable adsorption energy calculations. A vacuum region of approximately 15–18 Å was introduced along the direction perpendicular to the surface to prevent artificial interactions between periodically repeated slabs. The chosen slab thickness, vacuum spacing, k-point sampling, and supercell size are consistent with computational setups commonly adopted in previous DFT studies (Bligaard et al., 2004; Neugebauer & Scheffler, 1992; Ren et al., 2021) of adsorption on metal surfaces. These parameters ensure reliable convergence of the calculated energies and provide a reasonable balance between computational accuracy and efficiency for adsorption calculations on metallic surfaces. During structural relaxation, the bottom three layers of the nickel slab were fixed to mimic bulk-like behavior, while the upper three layers and the methane molecule were fully relaxed. Electronic states were described using a Localized Atomic Orbital (LCAO) basis set. A Double-Zeta Polarized (DZP) basis set was employed for carbon and hydrogen atoms, while nickel atoms were also treated using a DZP basis to properly describe the Ni 3d electronic states. Brillouin-zone integrations were carried out using a Monkhorst–Pack (Monkhorst & Pack, 1976) k-point grid of 4×4×1. A real-space mesh cutoff energy of 150 Ry was used to ensure accurate convergence of total energies and charge densities. Geometry optimization was performed using the Quasi-Newton algorithm until the maximum residual force on each atom was less than 0.02 eV/Å. Prior to adsorption calculations, the methane molecule was first

optimized in the gas phase to obtain its equilibrium geometry. The optimized CH_4 molecule was then placed above the Ni(111) surface at an initial distance of approximately 2.5–3.0 Å. To avoid artificial lateral interactions, only one methane molecule was introduced within each supercell. After structural relaxation of the combined system, total energies were calculated for the isolated methane molecule, the clean Ni(111) slab, and the CH_4/Ni(111) system. These energies were then used to compute the adsorption energy according to Eq. (1). In addition, Bader charge analysis was performed to evaluate the possible charge redistribution between the methane molecule and the nickel surface. The overall computational workflow adopted in this study, including surface construction, geometry optimization, adsorption energy calculation, and Bader charge analysis, is schematically illustrated in Figure (1).

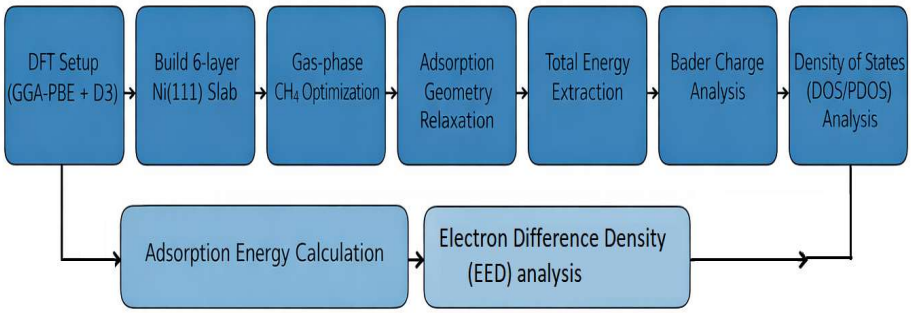

Figure (1). Schematic representation of the computational workflow employed in this study

The computational workflow begins with the DFT setup using the GGA-PBE functional including D3 dispersion corrections. A six-layer Ni(111) slab model was constructed and the methane molecule was optimized in the gas phase. Subsequently, the adsorption geometry of the CH_4/Ni(111) system was fully relaxed. After structural optimization, total energies were extracted to calculate the adsorption energy. Bader charge analysis was then performed to quantify charge transfer between the adsorbate and the surface. Finally, electronic structure analyses including density of states (DOS/PDOS) and electron density difference (EED) maps were computed to reveal the electronic interaction and charge redistribution at the adsorption Ni(111) interface.

Periodic boundary conditions were applied in all directions during the simulations. These computational parameters ensure reliable convergence and are consistent with commonly used DFT approaches for adsorption studies on metallic surfaces.

5. RESULTS

5.1. Optimized adsorption geometry

The optimized adsorption structure of the CH4 molecule on the Ni(111) surface is presented in Figure (2). After structural relaxation, the methane molecule maintains its tetrahedral geometry, with C–H bond lengths remaining close to 1.11 Å. The equilibrium distance between the carbon atom and the Ni surface is approximately 3.21 Å. The Ni–Ni interlayer distance changes only slightly from 2.49 Å to 2.48 Å, indicating that the metallic slab maintains its structural stability during methane adsorption. The

internal geometry of the methane molecule remains almost unchanged. A comparison of interatomic distances before and after geometry optimization is summarized in Table (1).

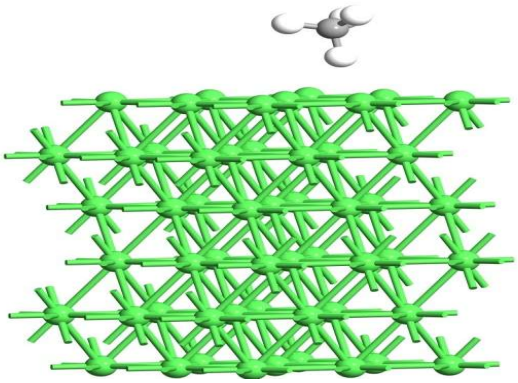

Figure (2). Optimized atomic configuration of the CH_4 adsorbed on a six-layer Ni(111) slab model.

Optimized adsorption configuration of the CH_4 molecule on the Ni(111) surface showing the relative position of the methane molecule with respect to the surface atoms

Table (1). Interatomic distances before and after relaxation for CH_4/Ni(111)

Bond	Initial/Relaxed distance (Å)	Literature range (Å)	References
Ni–Ni	2.49/2.48	2.48–2.50	–
H–H	1.80/1.81	1.80–1.82	–
C–H	1.10/1.11	1.10–1.11	–
C–Ni	3.06/3.21	3.10–3.30	(Arevalo et al., 2017; Ren et al., 2021; Yan et al., 2025; Shirazi, et al., 2017; Zhang, et al.,2017)
H–Ni	2.05/2.19	2.10–2.25	(Arevalo et al., 2017; Shirazi, et al., 2017)

The initial parameters were Ni–Ni = 2.49 Å, H–H = 1.80 Å, C–H = 1.10 Å, C–Ni = 3.06 Å, and H–Ni = 2.05 Å. After relaxation, the values change slightly to Ni–Ni = 2.48 Å, H–H = 1.81 Å, C–H = 1.11 Å, C–Ni = 3.21 Å, and H–Ni = 2.19 Å. These results show that the methane molecule retains its structural integrity while adsorbed on the Ni(111) surface.

5.2 Adsorption energy

The adsorption energy (E_{ads}) serves as a key quantitative parameter for evaluating the interaction strength between the methane molecule and the Ni(111) surface. In the present work, E_{ads} was determined according to Eq. (1) described in Section 2, based on the calculated total energies of the isolated methane molecule, the clean Ni(111) slab, and the combined CH4/Ni(111) system. The obtained values are $E_{tot}(CH_4)$=−220.86634 eV, E_{tot}(Ni(111))=−61032.45909eV, and $E_{tot}(Ni(111)+CH_4)$=−61252.10768 eV. Substitution of these energies into Eq. (1) yields an adsorption energy of E_{ads} = −1.21775 eV. The calculated adsorption energy indicates energetically favorable adsorption of methane on the Ni(111) surface.

Figure 3 shows the comparison of interatomic distances before and after geometry optimization.

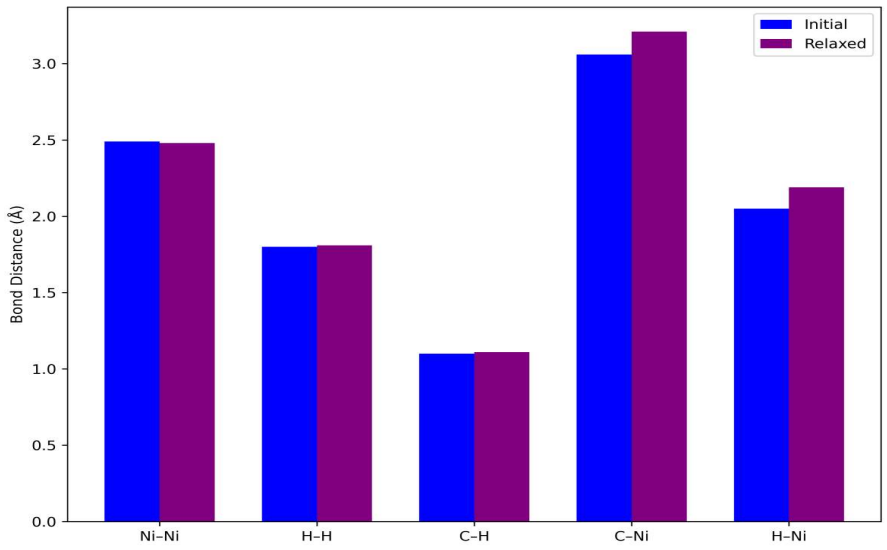

Figure (3). Comparison of bond distances before and after structural relaxation.

Table 2 summarizes previously reported adsorption energies for methane on Ni-based surfaces and compares them with the value obtained in this study. Earlier studies report adsorption energies in the range of approximately −0.10 to +0.05 eV. In the present work, the calculated adsorption energy for CH_4 on the Ni(111) surface is −1.22 eV, indicating energetically favorable adsorption and suggesting a weak interaction between the methane molecule and the Ni surface.

Optimized structure of the CH4/Ni(111) adsorption system illustrating the equilibrium adsorption geometry obtained after full structural relaxation.

Table (2). Comparison of CH_4 adsorption energies on Ni(111) with literature

System	Method / Functional	Reported Eads (eV)	Ref.
CH_4 on Ni(111)	DFT–PBE	+0.05 to −0.05	(Arevalo et al.,2017)
CH_4 on Ni surface	DFT–PBE/D2	−0.10	(Zhai et al.,2021)
CH_4 on Ni/MgO	DFT–PBE	−0.08	(Yan et al., 2025)
CH_4 pre-activation on Ni(111)	Mechanistic review	weak physisorption	(Ren et al., 2021)
CH_4 on Ni(111) — this work	DFT–PBE (2023)	−1.22	—

The difference between the adsorption energy obtained in the present study and values reported in previous theoretical works may arise from differences in computational parameters, including the slab thickness, supercell size, dispersion corrections, and the specific adsorption configuration considered. Despite these variations, the DOS and EED analyses consistently indicate weak electronic interaction between methane and the Ni(111) surface, confirming the physisorption nature of the adsorption process.

5.3 DOS analysis

To further investigate the electronic interaction between the methane molecule and the Ni(111) surface, the total and projected density of states (DOS) were calculated. The results indicate that the electronic states near the Fermi level are dominated by Ni 3d orbitals, while the contribution from methane orbitals remains very small. The absence of significant orbital hybridization between C 2p and Ni 3d states confirms the weak physisorption nature of methane on the Ni(111) surface.

Figure 4 presents the spin-polarized total density of states (TDOS) for the pristine Ni(111) surface and the CH_4/Ni(111) adsorption system. The Fermi level (E_F) is indicated by the dashed vertical line at 0 eV. The positive and negative regions correspond to spin-up and spin-down states, respectively. The electronic states of the clean Ni(111) surface are mainly dominated by Ni 3d orbitals, which produce prominent peaks near the Fermi level. After methane adsorption, the TDOS profile of the CH_4/Ni(111) system shows only very small modifications compared with the pristine Ni(111) surface. The contributions originating from methane are extremely weak and appear mainly in the energy region below the Fermi level. The absence of significant changes in the electronic states near the Fermi level indicates that methane adsorption does not strongly perturb the electronic structure of the Ni(111) surface. Moreover, no noticeable hybridization between methane molecular orbitals and Ni surface states is observed. These results confirm that the interaction between methane and the Ni(111) surface is governed by weak physisorption rather than chemisorption.

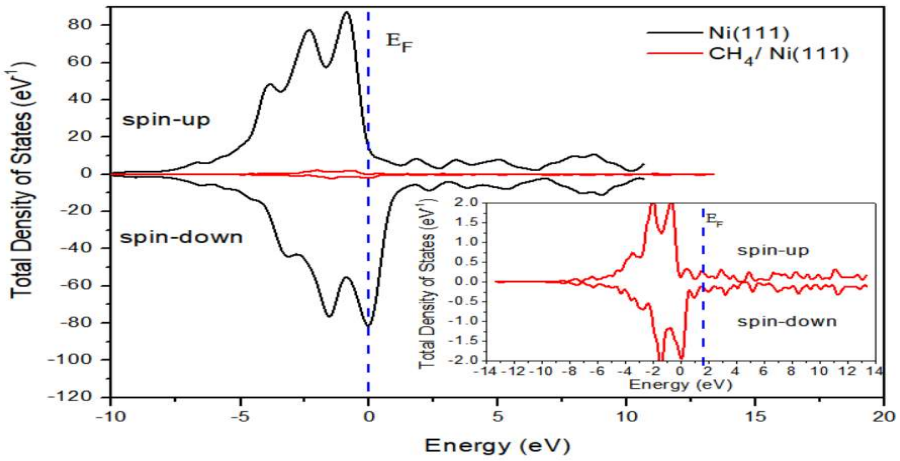

Figure (4). Spin-polarized total density of states (TDOS) of pristine Ni(111) and the CH_4/Ni(111) adsorption system. The dashed vertical line indicates the Fermi level (E_F) set at 0 eV.

Figure 5 presents the spin-polarized projected density of states (PDOS) of the CH_4/Ni(111) adsorption system. The electronic states near the Fermi level are mainly dominated by Ni d orbitals, indicating that the metallic surface largely governs the electronic structure of the system. The C p and H s states originating from the methane molecule are mainly located in deeper energy regions and show only weak contributions near the Fermi level. Moreover, the absence of significant overlap between Ni d states and methane orbitals suggests that strong orbital hybridization does not occur. These results

indicate that methane adsorption on the Ni(111) surface is governed by weak physisorption interactions rather than chemisorption.

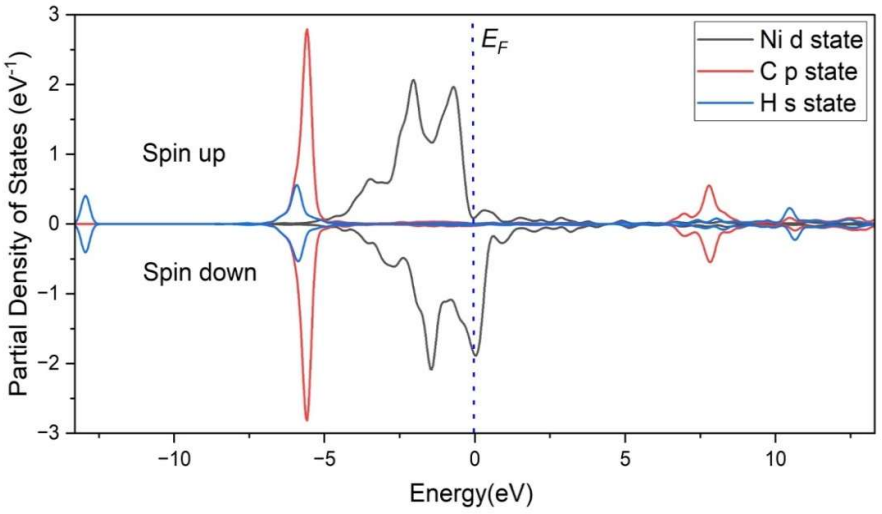

Figure (5). Spin-polarized projected density of states (PDOS) for the CH_4/Ni(111) adsorption system showing the contributions of Ni d, C p, and H s orbitals. The dashed vertical line indicates the Fermi level (E_F) set at 0 eV.

5.4 Bader charge analysis

Bader charge analysis was performed to investigate charge redistribution between the methane molecule and the Ni(111) surface. The results indicate that the carbon atom exhibits a small positive charge of approximately +0.13 e, while hydrogen atoms show small charge variations ranging from −0.08 e to +0.02 e. These small variations demonstrate that the methane molecule undergoes only negligible charge redistribution upon adsorption on the Ni(111) surface. The overall charge of the methane molecule remains nearly neutral, confirming that the interaction between CH_4 and the Ni surface is weak and does not involve significant charge transfer.

Figure 6 illustrates the calculated Bader charge variations for the atoms of the methane molecule adsorbed on the Ni(111) surface.

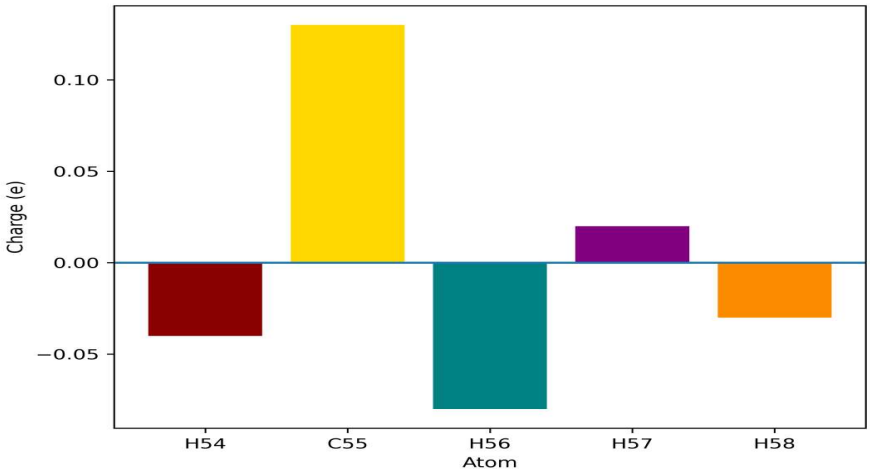

Figure (6). Bader charge differences for atoms of the CH_4 molecule adsorbed on the Ni(111) surface, illustrating the charge transfer between methane and the nickel surface after adsorption.

5.5 EED analysis

The EED method is widely used in surface science studies to visualize the redistribution of electronic charge that occurs upon adsorption. This analysis allows the identification of regions of charge accumulation and charge depletion in the adsorption system, thereby providing valuable information about the nature of the interaction between the adsorbate and the surface. In particular, the EED results help to determine whether the adsorption process is governed by strong chemical bonding accompanied by significant charge transfer or by weak physisorption interactions with minimal electronic redistribution. Therefore, the EED analysis complements the adsorption energy, Bader charge, and density of states (DOS) calculations and provides a more comprehensive understanding of the adsorption mechanism of CH_4 on the Ni(111) surface.

To further understand the electronic interaction between the methane molecule and the Ni(111) surface, the electron density difference (EED) analysis was performed. This method is commonly used in surface adsorption studies to visualize the redistribution of electronic charge induced by the interaction between an adsorbate and a substrate.

The EED results for the CH_4/Ni(111) system are illustrated in Figure (7). The red regions indicate electron accumulation, whereas the blue regions represent electron depletion resulting from methane adsorption on the Ni(111) surface, revealing the charge redistribution and interfacial interaction between the CH_4 molecule and the Ni substrate. The small redistribution of charge around the adsorption region suggests that only a weak interaction occurs between the methane molecule and the nickel surface, confirming the physisorption nature of the adsorption process. The visualization allows the identification of charge accumulation and charge depletion regions that appear upon adsorption. The charge redistribution is mainly localized around the Ni surface atoms in the vicinity of the methane molecule. Only a small amount of electron density rearrangement is observed between the methane molecule and the Ni(111) surface. The limited charge transfer between the adsorbate and the substrate

indicates that methane interacts weakly with the Ni(111) surface. This behavior is consistent with the adsorption energy, Bader charge analysis, and density of states (DOS) results, which collectively suggest that methane adsorption on the Ni(111) surface is governed primarily by weak physisorption interactions rather than strong chemical bonding.

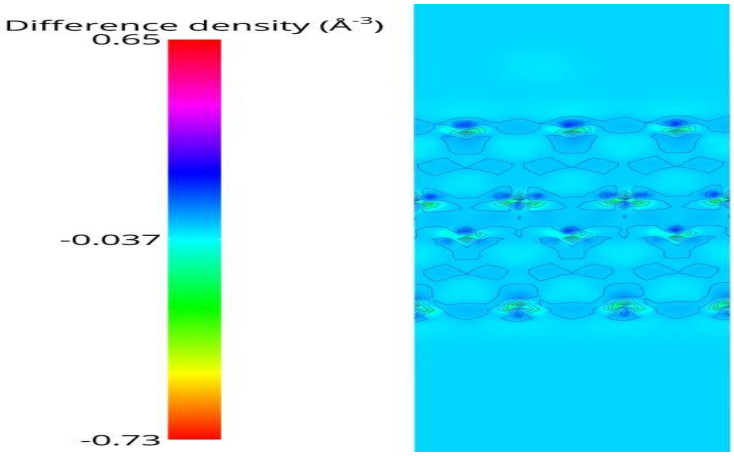

Figure (7). Electron density difference (EED) of the CH_4/Ni(111) adsorption system. Red and yellow regions indicate electron accumulation, whereas blue and cyan regions represent electron depletion

6. DISCUSSION

Unlike many previous studies focusing mainly on methane activation or catalytic decomposition, the present work provides a comprehensive electronic structure analysis of methane adsorption on the Ni(111) surface by combining adsorption energetics with DOS, PDOS, Bader charge, and electron density difference analyses. The combination of adsorption energy calculations with DOS and EED analyses provides a more comprehensive understanding of the adsorption mechanism at the atomic scale. These findings provide important atomic-scale insight into the interaction between methane molecules and nickel surfaces. Such information is particularly relevant for understanding the stability of methane in contact with nickel-based materials used in LNG storage and transportation infrastructure.

It should be noted that the present calculations are performed within the framework of static DFT at 0 K. Therefore, the obtained results provide fundamental insight into the adsorption mechanism at the atomic scale rather than a direct simulation of temperature-dependent processes under LNG operating conditions. Such first-principles calculations are widely used as a reference approach for understanding adsorption behavior on metallic surfaces.

These current results are crucial in understanding the adsorption mechanism of methane at the surfaces of Ni(111). The structural optimization shows that the tetrahedral geometry of the methane molecule is maintained after adsorption, and C–H bond lengths are near 1.11 Å. Equilibrium distances between the carbon atom and Ni surface are about 3.21 Å, relatively high compared to the standard chemisorption distance. These adsorption distances are consistent with weak physisorption interactions dominated by

low-energy van der Waals forces rather than strong covalent bonds. Methane does not undergo C–H bond activation and deformation of the molecule due to the preservation of its molecular geometry during its adsorption. Similar phenomenon has been reported for methane adsorption on nickel surfaces in previous hypothetical research. For instance, Arevalo et al. (2017) showed that methane adsorption on Ni(111) is achieved by weak interactions and does not initiate any C–H bond activation. The current structural results therefore follow with respect to previous density functional theory (DFT) studies well. This work estimated an adsorption energy (E_{ads} = −1.22 eV), indicating energetically favorable adsorption of methane on the Ni(111) surface. Although the calculated adsorption energy differs somewhat from values reported in previous studies, the DOS and EED analyses clearly indicate weak electronic interaction and negligible charge transfer between methane and the Ni(111) surface, confirming that the adsorption process remains within the physisorption regime. Notwithstanding variation of this value compared to some reported adsorption energies in the literature, the general interpretation does conform to what has previously been reported. DFT studies have shown that methane only interacts weakly with nickel surfaces. For example, Zhai et al. (2021) reported adsorption energies of around −0.10 eV for methane on Ni surfaces prior to this C–H bond activation process. Similarly, Yan et al. (2025) reported weak adsorption of methane on Ni/MgO catalytic systems with no methane dissociation shown before dissociation of methane. These results demonstrate that methane remains molecularly stable on close-packed Ni surfaces at low temperatures. Due to differences in computational conditions between this study and previously reported calculations (slab thickness, vacuum spacing, exchange–correlation functional, basis set selection), variations in the calculated adsorption energies can be observed. These methodological considerations render weakly interacting systems highly sensitive in terms of adsorption energy values. Thus, a difference in numerical values does not mean a different adsorption mode, but rather differences in computational approaches. The electronic structure analyses provide further insight into the adsorption mechanism of methane on the Ni(111) surface. The total and projected density of states (DOS) results reveal that the electronic states near the Fermi level are mainly dominated by Ni 3d orbitals, while the contributions from methane orbitals remain very weak. The absence of significant overlap between Ni 3d and methane-related states indicates that strong orbital hybridization does not occur upon adsorption. Additional details on adsorption mechanism are presented in the Bader charge analysis. It is possible to view, from both the above findings, that the transfer of total charge between the methane and the Ni(111) surface is small. Carbon atom has a slight addition of positive charge and differences of hydrogen are negligible. As a result, the overall charge redistribution in the methane molecule is almost zero, indicating the structure of the molecule stays in its electronic arrangement after adsorption. Other surfaces have shown similar results for methane adsorption based on analogous observations. Ren et al. (2019) studied methane adsorption on MoX_2 monolayers and reported the interaction is dominated by weak van der Waals forces, with negligible charge redistribution. Zhang et al. (2017) demonstrated the very small adsorption energies and an immiscible charge transfer on graphene methane adsorption of carbon-based chemistries (Zhang et al., 2017).

In addition, the electron density difference (EED) analysis shows only a small redistribution of electronic charge around the adsorption region. Minor charge accumulation is observed near the surface Ni atoms,

accompanied by slight charge depletion around the methane molecule. This limited charge transfer suggests that the interaction between CH_4 and the Ni(111) surface is relatively weak. The combined DOS and EED results therefore confirm that methane adsorption on the Ni(111) surface is governed primarily by weak physisorption interactions rather than strong chemisorption. These findings are also consistent with the calculated adsorption energy and Bader charge analysis, which indicate minimal electronic perturbation of the Ni(111) surface upon methane adsorption. Because methane interacts weakly with the Ni(111) surface, the adsorption energy differences between possible adsorption sites are expected to be very small, indicating limited site selectivity typical for physisorption systems.

These studies indicate that in the absence of catalytic activation sites methane adsorption generally follows weak dispersion-driven behavior. The weak adsorption energy and minimal charge transfer and the structural stability of the Ni slab also support the physisorption mechanism. The Ni–Ni interlayer distances are observed to be nearly unchanged after adsorption, suggesting that the metallic surface retains a bulk-like structure with little lattice distortion or surface reconstruction. These results combining structural, energetic, and electronic analyses confirm that methane, adsorbed at the Ni(111) surface is primarily governed weak physisorption rather than chemisorption. The methane molecule remains chemically inactive and electrically stable upon nickel surface interaction. These results are in agreement with previous theoretical and experimental studies, and show that methane activation on nickel surfaces usually needs elevated temperatures consistent with catalytic reforming processes (Ren et al., 2021).

7. CONCLUSION

In this work, the adsorption performance of methane on the Ni(111) surface was systematically studied based on first-principles density functional theory (DFT) calculations. The optimized adsorption geometry demonstrates that the methane molecule preserves its ideal tetrahedral structure with nearly identical C–H bond lengths as the isolated molecule. The molecular distance to the nickel surface (equilibrium distance between the carbon atom and the nickel surface) is ~3.21 Å, which indicates weak interaction between the metallic substrate. Furthermore, the interlayer distances between Ni and Ni hardly budge, demonstrating that methane-based adsorption has not made structural disturbance or redesign of the Ni(111) surface. The adsorption energy (E_{ads} = −1.22 eV), calculated from the total energy values obtained from DFT calculations, indicates energetically favorable adsorption of methane on the Ni(111) surface. The result showed that methane is not making chemical bonds with the clean nickel surface and it rather encounters the nickel surface using dispersion force. The amount of adsorption energy varies from some earlier experimental results, but overall, its interpretation has been consistent with theoretical data which have characterized methane adsorption on Ni surfaces as weak physisorption. The DOS and PDOS analyses reveal that the electronic structure near the Fermi level is primarily governed by Ni 3d states, while the contributions from methane orbitals remain minimal. The absence of significant orbital hybridization between Ni and methane states confirms that methane adsorption on the Ni(111) surface occurs through weak physisorption interactions. Bader charge analysis corroborates this finding as it shows the little charge transfer between methane and the nickel slab. The electron structure of the methane molecule is kept and there is only mild charge polarization

at the interface. The EED results show limited charge accumulation and depletion around the adsorption region, confirming that methane interacts weakly with the Ni(111) surface and remains largely in a non-reactive molecular state. These results testify to the chemically and electronically inert nature of methane on the Ni(111) surface in the studied environment. In general, the results show that the interaction between methane and Ni(111) surface only has weak van der Waals force and no chemisorption, or C–H bond activation is observed. The insights obtained from these observations afford valuable atomistic insight into the interactions between methane and nickel, and the contribution to the understanding of stability of methane in nickel (nickel-based) materials employed in liquefied natural gas (LNG) storage and transportation systems.

These findings contribute to a better understanding of methane–metal surface interactions and may assist in evaluating the reliability of nickel-based materials used in LNG storage and cryogenic energy technologies.

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REFERENCES:

Arevalo, R. L., Poloni, R., & Matanović, I. (2017). Tuning methane decomposition on stepped Ni surfaces: Role of subsurface atoms. Scientific Reports, 7, 14050. https://doi.org/10.1038/s41598-017-14050-3

Bligaard, T., Nørskov, J. K., Dahl, S., Matthiesen, J., Christensen, C. H., & Sehested, J. (2004). Brønsted–Evans–Polanyi relations in heterogeneous catalysis. Journal of Catalysis, 224(1), 206–217. https://doi.org/10.1016/j.jcat.2004.02.034

Boukhvalov, D. W., & Katsnelson, M. I. (2008). Chemical functionalization of graphene with defects. Nano Letters, 8(12), 4373-4379. https://doi.org/10.1021/nl802234n

BP. (2023). Statistical review of world energy. BP Energy Economics.

Henkelman, G., Arnaldsson, A., & Jónsson, H. (2006). A fast and robust algorithm for Bader decomposition of charge density. Computational Materials Science, 36(3), 354–360. https://doi.org/10.1016/j.commatsci.2005.04.010.

Hohenberg, P., & Kohn, W. (1964). Inhomogeneous electron gas. Physical Review, 136(3B), B864–B871. http://dx.doi.org/10.1103/PhysRev.136.B864

Gao, L., Wang, J., Binama, M., Li, Q., & Cai, W. (2022). The design and optimization of natural gas liquefaction processes: A review. Energies, 15(21), 7895. https://doi.org/10.3390/en15217895

Koh, E. W. K., Chiu, C. H., Lim, Y. K., Zhang, Y. W., & Pan, H. (2012). Hydrogen adsorption on and diffusion through MoS_2 monolayer: First-principles study. International Journal of Hydrogen Energy, 37(19), 14323–14328. https://doi.org/10.1016/j.ijhydene.2012.07.069

Martin, R. M. (2004). Electronic structure: Basic theory and practical methods. Cambridge University Press.

Mokhatab, S., Poe, W. A., & Speight, J. G. (2014). Handbook of liquefied natural gas. Elsevier.

Monkhorst, H. J., & Pack, J. D. (1976). Special points for Brillouin-zone integrations. Physical Review B, 13(12), 5188–5192. https://doi.org/ppptrrujjj10.1103/PhysRevB.13.5188

Neugebauer, J., & Scheffler, M. (1992). Adsorbate–substrate interactions via total-energy calculations. Physical Review B, 46(24), 16067–16080. https://doi.org/10.1103/PhysRevB.46.16067

Perdew, J. P., Burke, K., & Ernzerhof, M. (1996). Generalized gradient approximation made simple. Physical Review Letters, 77(18), 3865–3868. https://doi.org/10.1103/PhysRevLett.77.3865

Ren, J., Liu, H., Xue, Y., & Wang, L. (2019). Adsorption behavior of CH_4 gas molecule on the MoX_2 (S, Se, Te) monolayer: The DFT study. Nanoscale Research Letters, 14, 293. https://doi.org/10.1186/s11671-019-3125-5

Ren, Y., Liu, X., Zhang, Z., & Shen, X. (2021). Methane activation on single-atom Ir-doped metal nanoparticles from first principles. Physical Chemistry Chemical Physics, 23(29), 15564–15573. https://doi.org/10.1039/D1CP02022F

Sehested, J., Gelten, J. B., & Helveg, S. (2004). Sintering of nickel catalysts under methane steam reforming conditions. Journal of Catalysis, 223(2), 432–443. https://doi.org/10.1016/S0021-9517(03)00075-7

Shirazi, M., Dehghan, G., & Neyts, E. C. (2017). DFT study of Ni-catalyzed plasma dry reforming of methane. Journal of Molecular Catalysis A: Chemical, 426, 473–482. https://doi.org/10.1016/j.apcatb.2017.01.004

Wang, J., & Wang, G.-C. (2024). Mechanisms of CH_4 activation over oxygen-preadsorbed transition metals by ReaxFF and AIMD simulations. Journal of Computational Chemistry, 45(5), 238–246. https://doi.org/10.1002/jcc.27233

Wang, K., Zhao, S., & Wang, Z. (2025). Global liquefied natural gas market development and future outlook. Natural Gas Industry B, 12(5), 636–646. https://doi.org/10.1016/j.ngib.2025.10.001

Yan, X., Wang, R., Yue, F., Wang, R., Zhang, H., Li, J., Peng, W., & Zhang, J. (2025). High performance Ni-MgO (111) nanosheet catalysts for CO_2 reforming with methane. Fuel, 385, 134176. https://doi.org/10.1016/j.fuel.2024.134176

Zhai, Z., Lu, J., Wang, H., & Xu, Y. (2021). Ni-based catalysts for low-temperature methane activation: DFT and experiments. Applied Catalysis B, 292, 120145. https://doi.org/10.3390/catal3020563

Zhang, W., Li, Y., & Chen, Z. (2017). Methane adsorption on graphene: A first-principles study. Carbon, 120, 287–295. https://doi.org/10.1016/j.susc.2011.01.012

Zonfrilli, M., Facchino, M., Serinelli, R., Chesti, M., De Falco, M., & Capocelli, M. (2023). Thermodynamic analysis of cold energy recovery from LNG regasification. Journal of Cleaner Production, 420, 138443. https://doi.org/10.1016/j.jclepro.2023.138443 83