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COMMUNICATION

First-Principles Insights into the Direct Synthesis of Acetic Acid from CH₄ and CO₂ over TM-Si@2D CatalystsMingyuan Zhang,^a Linxia Cui,^a Yang Jiang,^a Rui Gao,^a Haigang Hao^{*a} and Meilan Huang^{*b}Received 00th January 20xx,
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The direct synthesis of acetic acid from natural gases has attracted great attention. However, achieving selective C–C coupling remains a major challenge. We designed doped single-atom transition metal catalysts on 2Ds materials, guided by DFT calculations on the reaction pathways for acetic acid synthesis via CH₄/CO₂ coupling. Among the catalysts examined, Ni-Si@h-BN shows strong electron synergy in CH₄ activation and C–C coupling under the E–R mechanism, confirmed by kinetics.

Transforming CH₄ and CO₂ into acetic acid offers a green route to convert greenhouse gases into value-added chemicals¹. Understanding the reaction mechanism is essential for catalyst design: CH₄ first dissociates into CH₃^{*} and H^{*}, after which CH₃^{*} couples with CO₂ to form CH₃COO^{*}. This intermediate undergoes hydrogenation to yield CH₃COOH, which subsequently desorbs as acetic acid². Homogeneous catalysts like Pd(OAc)₂/Cu(OAc)₂/K₂S₂O₈/CF₃COOH³, RhCl₃⁴ and PdSO₄⁵ have been used for this conversion but it is challenging to recycle the catalysts. More practical heterogeneous catalysts use supports like TiO₂, Al₂O₃, SiO₂ and zeolites, with active sites such as Zn or Cu⁶. For instance, Cu-K-ZSM-5 zeolite⁷ converts CH₄ and CO₂ to acetic acid at 500°C, achieving 5% CH₄ conversion and 100% acetic acid selectivity after 1 hour, while ZnO-CeO₂ supported on montmorillonite⁸ achieves 8.33% CH₄ conversion and 100% selectivity at 300°C. Zn-based catalysts generally show higher activity than Cu-based ones but they still require stringent conditions for effective activation⁹. Theoretical calculations can underpin experimental efforts to improve catalyst activity by revealing reaction pathways and energy barriers. In particular, understanding the elementary steps of C–H activation and subsequent C–C coupling is especially important for the direct synthesis of acetic acid catalysts¹⁰. Langmuir-Hinshelwood (L-H) and Eley-Rideal (E-R) mechanisms are two commonly adopted mechanisms for CO₂–CH₃^{*} coupling. Nie et al.¹¹ found that Fe/ZnO₂ catalysts activate

CH₄ efficiently due to Fe–Zn bimetallic synergy, with low barriers for CH₄ activation (0.30 eV) and C–C bond formation (0.75 eV) via the L-H pathway. However, the L-H mechanism requires dual adsorption sites, which increases the probability of side reactions¹². The E–R mechanism, involving reactions between gas-phase molecules and adsorbed species, usually reflects experimental conditions¹³. When CH₄ and CO₂ compete for adsorption sites, the relative adsorption strengths govern which pathway becomes dominant. In Zn-ZSM-5 catalysts¹⁴, CH₄ preferentially adsorbs on Zn²⁺ sites to form CH₃^{*} intermediates, while CO₂ shows weak affinity (<0.2 eV), thus gas-phase CO₂ couples directly with adsorbed CH₃ following an E–R mechanism. Although Zn-ZSM-5 lowers the barriers for CH₄ activation (0.65 eV) and acetate formation (0.20 eV), its C–C coupling activity remains limited (1.79 eV), underscoring the need to exploit selective C–C bond formation by other transition metal catalysts under E–R pathway. Catalysts with well-defined single-site active units¹⁵—such as isolated metal atoms with specific coordination environments or tailored metal–support interfaces—are highly promising for enhancing C–C coupling via the E-R mechanism.

Nickel is commonly used for CH₄ conversion due to its high activity, but it is prone to coking and sintering¹⁶. Studies show that adding Si atoms in Ni-Si/ZrO₂ catalysts enhances Ni dispersion, stability, and resistance to coking during CH₄ and CO₂ dry reforming¹⁷. This inspired us to examine the effect of Si on the electron density of Ni-based catalysts, to optimize Ni sites for coupling CH₄ and CO₂ into acetic acid. On the other hand, single-atom catalysts (SACs) on 2D materials have shown significant potential for CO₂ conversion, owing to their high atom utilization and activity, for example, Feng *et al.* demonstrated that SACs embedded in 2D graphitic carbon nitride support exhibit high catalytic efficiency¹⁸. For example, Zn-based metal oxide SACs show unique catalytic properties for converting CH₄ and CO₂ to acetic acid; however, efficient C–C coupling remains a challenge¹⁹. The high surface area and stability of two-dimensional (2D) materials enable SACs@2D systems with well-defined active centres, surpassing conventional metal oxide supports²⁰ and potentially improving C–C coupling. Herein, we designed SACs composed of transition metals (Mn, Fe, Co, and Ni) doped with Si promoters on h-BN

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(TM-Si@h-BN) to identify optimal active component. Subsequently, we evaluated various 2D materials, including graphene (GR), N₄-doped graphene (N₄@GR), and phosphorene (P), to determine the optimal catalyst configuration. We demonstrated that Ni-Si@h-BN is a promising alternative to traditional catalysts and elucidated its activation and reaction mechanism: electron transfer from Si to Ni creates an electron-rich Ni site (Ni^{δ-}) and its moderate work function is favourable for electron balance, facilitating CH₄ activation and CO₂ adsorption.

The computed binding energy (E_b) and formation energy (E_f)²¹ for TM-Si@h-BN catalysts demonstrate the stability of Si and TM atoms on h-BN (Table S1). AIMD simulations of the TM-Si@h-BN catalysts structure at 500 K demonstrate its thermodynamic stability (Fig. S1a, b). Bader charge calculations (Table S1) show electrons transfer from Si to transition metals, forming a TM₁^{δ-}-Si₁^{δ+} distribution. We compared the adsorption abilities of CH₄ and CO₂ at 500 K. Although both CH₄ and CO₂ exhibit relatively weak interactions with the surfaces, CH₄ binds more strongly (-0.36 ~ 0.15 eV) than CO₂ (0.22 ~ 0.65 eV) on all TM-Si@h-BN catalysts, underscoring that CH₄ is preferentially activated across these materials (Fig. S1c, d). The work function (Fig. S2), reflecting the electron transfer ability of TM-Si@h-BN, controls CH₄ and CO₂ adsorption such that CH₄ adsorption weakens with increasing work function, while CO₂ adsorption strengthens (Fig. S3a).

respectively. On Co-Si@h-BN, H* prefers the Co-Si bridge site, with a higher barrier of 0.96 eV. On Ni-Si@h-BN, the hydrogen atom migrates to the top site of Si, incurring an energy barrier of 0.50 eV. **The C-C coupling** is initiated by the reaction of CH₃* and gaseous CO₂, forming the CH₃COO* intermediate at TM sites via the E-R mechanism. Ni-Si@h-BN shows the lowest barrier for this step (0.71 eV) among the TM-Si@h-BN catalysts, and crystal Hamilton population (COHP) analysis reveals a weaker Ni-CH₃ bond (integrated strength ICOHP: -1.18 eV) that facilitates CO₂ insertion (Fig. S7). **The hydrogenation of CH₃COO* to acetic acid** generally proceeds with high barriers on TM-Si@h-BN. Furthermore, the energetic span model (δE) was employed as a direct descriptor of the catalytic cycle rate²². At 500 K, except for Mn-Si, where TS3 (CH₃COO* hydrogenation) is the turnover-determining transition state (TDTS), TS2 (C-C coupling) serve as the TDTS for the other TM-Si systems exhibit, while CH₃COO* + H* act as the turnover-determining intermediate (TDI) in all cases. The corresponding δE values for each system are summarized in Table S12. Notably, Ni-Si@h-BN shows the lowest δE (1.26 eV), emphasizing its superior activity and highlighting its potential as a 2D support for further optimization.

The structural stability of Ni-Si@2D and the thermodynamic stability of Ni-Si@2D at 500 K are confirmed (Fig. S8). Bader charge analysis reveals that silicon donates electrons to transition metals on both Ni-Si@2D and TM-Si@h-BN catalysts, highlighting its general role as an electron donor (Table. S5), and accounting for the stronger CH₄ adsorption observed on TM-Si@2D compared to TM@2D (Table S7).

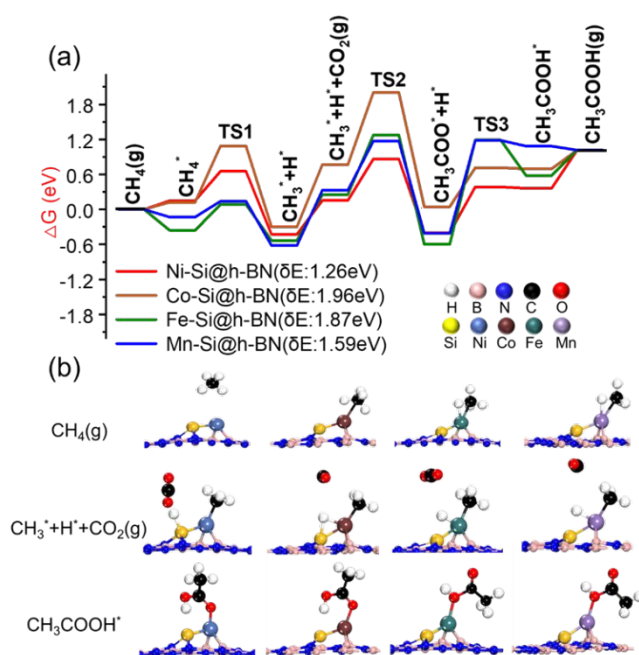


Fig 1. The coupling of CH₄ and CO₂ into acetic acid on TM-Si@h-BN at 500 K. (a) Reaction energy profile (energy span, δE is shown in parentheses). (b) Adsorption configurations of key reactants and products. See Fig. S6 and Table S4 for details.

The dissociation of CH₃* at TM sites is influenced by the presence of doped Si. On Mn-Si@h-BN and Fe-Si@h-BN, the H atom is co-adsorbed with CH₃* on the top site of TM, exhibiting low energy barriers of 0.27 and 0.44 eV (Fig. 1 and Table S4),

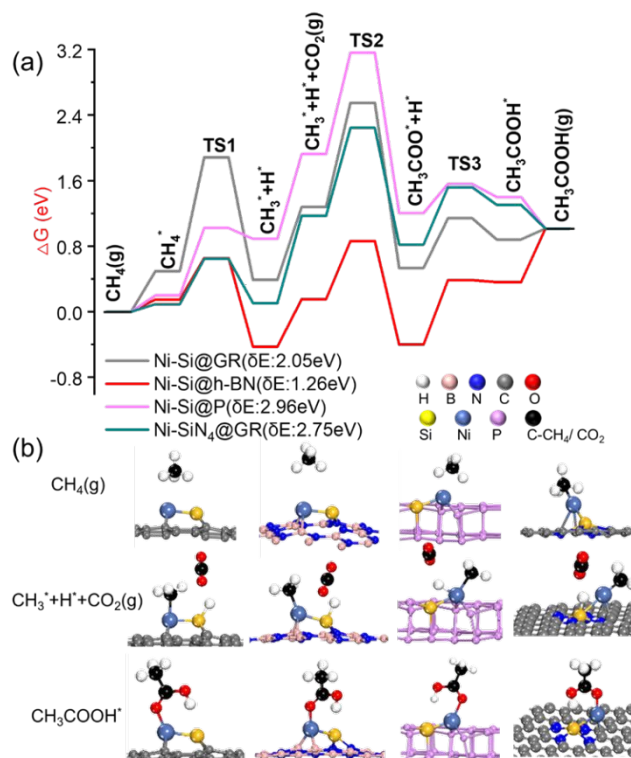


Fig 2. The coupling of CH₄ and CO₂ into acetic acid on Ni-Si@2D at 500 K. (a) Reaction energy profile (energy span, δE is shown



in parentheses). (b) Adsorption configurations of key reactants and products. See Fig. S9 and Table S9 for details.

The CH_4 adsorption energy on Ni-Si@2D strengthens with increasing work function, whereas the CO_2 adsorption energy exhibits a volcano-shaped trend (Fig. S3b). The Ni atom in Ni-Si@2D were identified as the primary activation site for **CH_4 dissociation** (Fig. 2 and Table S9), with Ni-Si@h-BN exhibiting the lowest barrier (0.50 eV), outperforming Ni-Si@GR, Ni-Si@P, and Ni-SiN₄@GR. The Bader charge analysis of **C-C coupling step** (Table S10) reveals that electron transfer from the CH_3 -TM bond to CO_2 , facilitating C-C bond formation. Ni-Si@h-BN exhibits a barrier of 0.71 eV for C-C coupling, which is comparable to other Ni-Si@2D systems and lower than reported E-R pathway catalysts¹⁹. **During acetic acid formation and desorption**, most hydrogenation reactions proceed easily on Ni-Si@2D. For Ni-Si@2D catalysts at 500 K, the energy span is smallest on h-BN (1.26 eV), indicating its superior activity. While TS2 (C-C coupling) is the TDTS across all systems, the TDI differs: it is $\text{CH}_3\text{COO}^* + \text{H}^*$ on Ni-Si@h-BN whereas it is adsorbed CH_4^* on the others. Together with fast CH_4 dissociation, facile C-C coupling, and favourable hydrogenation, Ni-Si@h-BN exhibits markedly enhanced activity compared with other reported catalysts (Table S11). By-product formation during acetic acid synthesis on Ni-Si@h-BN was also evaluated. Energetic span analysis shows that the C-C coupling pathway to CH_3COO^* ($\delta E = 0.71$ eV) is much more favorable than CO_2 hydrogenation routes via COOH or HCOO ($\delta E = 1.97$ and 0.81 eV), indicating C-C coupling dominates over formic acid formation (Fig. S12).

To further understand temperature effects, the energetic span was analysed at different temperatures, and the corresponding TDTS and TDI are summarized in Table S12. Ni-Si@h-BN exhibits the lowest δE across 300–900 K, reaching 1.23 eV at 600 K (Fig. S13). Based on the energetic span model, TOFs for acetic acid formation (300–900 K, 1 bar)²³ were calculated (Fig. 3), showing consistently highest TOFs for Ni-Si@h-BN, with a peak at 700 K ($8.02 \times 10^{-2} \text{ s}^{-1}$, logTOF: 2.90), after which TOFs decreases with further temperature increase. These results highlight Ni-Si@h-BN as an efficient catalyst for CH_4 and CO_2 conversion under moderate conditions while minimizing coke formation²⁴.

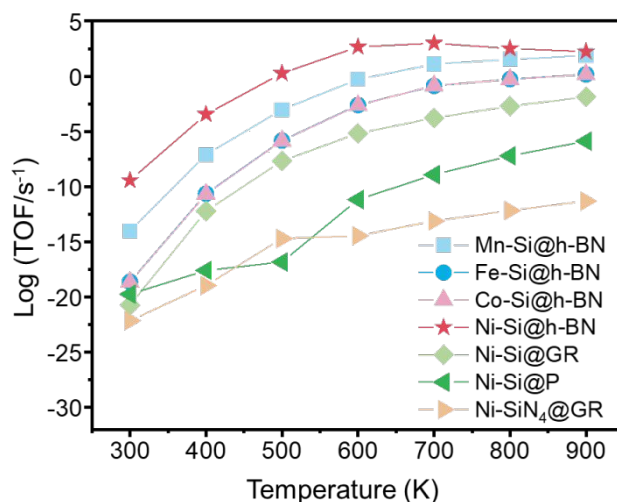


Fig. 3 Turnover frequencies for CH_3COOH production over TM-Si@2D as a function of temperature ($\text{CH}_4/\text{CO}_2 = 1:1$, 1 bar).

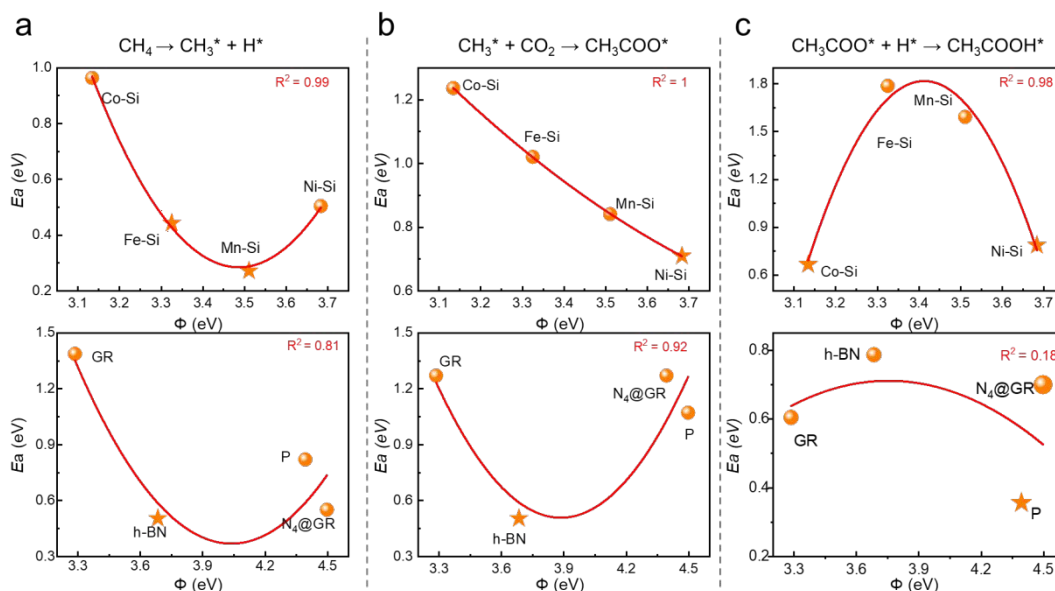


Fig. 4 Relationship between work function (Φ) and energy barriers (E_a) for acetic acid synthesis from CH_4 and CO_2 on TM-Si@2D at 500 K: (a) CH_4 dissociation; (b) C-C coupling; (c) acetic acid formation. Upper panel: the 2D material is h-BN, Lower panel: The transition metal is Ni-Si on different 2D materials.

Understanding the relationship between catalytic performance and electronic properties is crucial for designing new catalysts for efficient CH_4 - CO_2 coupling toward acetic acid. CH_4

dehydrogenation on TM-Si@2D exhibits a volcano dependence on work function (Fig. 4a), with the lowest barriers with moderate values (3.3–4.0 eV) due to optimal polarization of the



C–H bond. For C–C coupling (Fig. 4b), most TM–Si@2D follow a volcano-like behaviour, whereas TM–Si@h-BN shows a nearly linear decrease in barrier with increasing work function, benefiting from π back-donation that enhances CO₂ adsorption and facilitates CH₃* activation. In contrast, CH₃COO hydrogenation follows an inverse volcano relationship to the work function (Fig. 4c), showing reduced barriers at both low and high work function values. Bader charge analysis (Fig. S14) further confirms that higher TM electron density generally is attributed to reduced barriers throughout entire reaction process. Ni–Si@h-BN, characterized by an electron-rich Ni site (Ni^{-2.16}) and a moderate work function (3.68 eV), exhibits the lowest barrier in the rate-determining step and thus maintains thermodynamic favourability across all three elementary steps. This results from its balanced electron donation to the substrate with optimal adsorption strength.

We elucidated the acetic acid synthesis mechanism from CO₂ and CH₄ and designed TM–Si@2D based on DFT calculations. Silicon incorporation enriches transition metals with electrons, generating electron-rich active sites that enhance the catalytic activity. Ni–Si@h-BN stands out among doped transition metal catalysts. Its moderate work function and high Ni electron density facilitate CH₄ activation, while the Ni₁^{δ-}–Si₁^{δ+} synergy enables C–C coupling through the E–R mechanism. The turnover frequency for CH₄ and CO₂ conversion to acetic acid reaches $8.02 \times 10^{-2} \text{ s}^{-1}$ at 700 K and 1 bar, demonstrating the reaction's feasibility under practical conditions. This advantageous electronic structure underpins its capability for efficient and selective acetic acid synthesis.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supplementary Information.

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Data availability

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The data supporting this article have been included as part of the Supplementary Information.

