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Electronic and Geometric Effects of Dual-Atom Catalysts on C–C Coupling during CO₂ Reduction: Insights from Density Functional Theory and Interpretable Machine Learning

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Abstract

Dual-atom catalysts (DACs) offer unique opportunities for promoting C₂⁺ formation in CO₂ electroreduction; however, the roles of electronic and geometric structures in governing C–C coupling remain unclear. Herein, we systematically investigate eighty fourth-row transition-metal dimers anchored on N-doped graphene using density functional theory combined with interpretable machine learning. Our results demonstrate that both *CO and *OCCO adsorption strongly depend on the metal identity and metal–metal distance, exhibiting volcano-type or linear relationships that lead to regular variations in C–C coupling energies. To establish quantitative relationships between coupling energy and the electronic and geometric structures, we construct interpretable machine-learning models based on physically motivated descriptors. Feature screening and SISO analysis identify the number of metal valence electrons and the metal–metal distance as the dominant factors governing coupling energies. The resulting three-dimensional descriptor achieves good predictive performance, enabling rapid evaluation of DAC activity for the C–C coupling process. Overall, this study provides fundamental insights into the structure-activity relationships of DACs and offers a practical strategy for designing catalysts with enhanced C₂⁺ selectivity.

KEYWORDS: C–C coupling, Dual-atom catalysts, Structure-activity relationship, Density functional theory, Interpretable machine learning

1. Induction

CO₂ reduction reaction (CO₂RR) offers a promising strategy for mitigating excessive atmospheric CO₂ by converting it into value-added chemicals¹⁻³. C₂₊ products, in particular, are considered ideal targets for CO₂RR⁴; however, competition with C₁ products presents a significant challenge in achieving high selectivity for C₂ products⁵. Previous studies have demonstrated that the C–C coupling of C₁ intermediates plays a pivotal role in determining product distribution⁶⁻⁷. This process imposes stringent requirements on optimizing both the structure and electronic state of the catalysts⁸⁻¹⁰. Therefore, systematic investigation of these key factors is essential for guiding the rational design and fabrication of C₂₊ catalysts.

Owing to the atomic-level dispersion structure, single-atom catalysts (SACs) exhibit high atomic utilization efficiency and excellent catalytic activity¹¹, and have been widely applied in CO₂RR. However, the isolated nature of their active centers limits synergistic interactions, making it difficult to overcome intrinsic constraints associated with multimolecular reaction pathways. In contrast, dual-atom catalysts (DACs) provide adjacent active sites capable of simultaneously adsorbing multiple reactants and exploiting synergistic effects to optimize intermediate adsorption¹²⁻¹³. This feature breaks the linear scaling relationships commonly observed in SACs and offers a promising strategy for facilitating multimolecular reaction processes. Consequently, a variety of DACs have been designed and applied to CO₂RR. For example, Li et al. developed an Ag₂ dual-atom catalyst anchored on a graphene support with a well-defined AgN₃–AgN₃ coordination structure¹⁴. This catalyst achieved a high Faradaic efficiency for CO production and enhanced stability compared to SAC Ag/graphene and conventional Ag nanoparticles. Theoretical calculation revealed that the dual Ag sites synergistically stabilize *CO₂ intermediates by coordinating with both the C and O atoms, thereby lowering the energy barrier for *COOH formation. DACs also show unique advantages in CO₂ reduction to C₂ products. Precisely controlled bimetallic sites significantly promote C–C coupling via atomic-level synergy¹⁵⁻¹⁶. Sun et al. reported a nitrogen-coordinated di-copper catalyst (Cu₂/NC) capable of selectively generate C₂H₄ during CO₂RR¹⁷. Further theoretical analysis demonstrated that Cu–Cu bimetallic sites not only significantly enhance the adsorption of CO intermediates, but also reduce the C–C coupling energy barrier for CO dimerization, thereby promoting selective C₂H₄ formation.

The synergistic effects governing C–C coupling originate from the regulation of both electronic and geometric structures. From the electronic perspective, Singh et al. tuned the electronic structure of Ag–Co bimetallic catalysts¹⁸. The Ag–Co synergy not only enhanced the adsorption strength of the *CO intermediate, but also facilitated C–C coupling and deep hydrogenation through cooperative dual-site interactions. In addition, Gao et al. systematically investigate the electronic effects on the CO₂RR process through density functional theory (DFT)¹⁹. They identified three key factors for efficient C–C coupling: the interaction between metal sites and intermediates, orbital contributions of carbon in metal–

carbon bonds, and electrostatic repulsion between coupled carbon atoms. From the geometric perspective, the essential distinction between DACs and SACs lies in the spatial arrangement of metal sites. When the interatomic distance decreases to a critical threshold, synergistic DAC systems with enhanced catalytic performance emerge. Several studies indicate that CO species preferentially adsorb at the bridge site between the two metal atoms in DACs, predominantly leading to C₁ products, a behavior likely associated with the metal–metal distance. Kim et al. reported a Cu/Ni dual-atom catalyst (Cu/Ni–NC) anchored on N-doped carbon, in which a Cu–Ni distance of ~4.08 Å maximized synergistic interactions and significantly enhanced CO₂RR activity and CO selectivity²⁰. Similarly, Duan et al. modulated the interatomic distance of Cu dimers in a Cu-based boron imidazolate framework (BIF) by employing different anionic Cu salts. Compared with metallic Cu (2.53 Å), Cu-BIF/SO₄ (3.90 Å), and Cu-BIF/NO₃ (4.21 Å), the optimal Cu–Cu distance of 3.3 Å in Cu-BIF/Cl yielded a higher Faradaic efficiency for C₂₊ products¹⁰. These results highlight that C–C coupling is jointly governed by electronic and geometric structures in DACs. However, their synergistic interplay and optimal combinations remain poorly understood, underscoring the need for predictive catalyst design strategies.

In this work, we integrated DFT with interpretable machine learning to establish quantitative structure-activity relationships for the C–C coupling process on DACs. Fourth-row transition-metal dimers anchored on four types of nitrogen-doped graphene structures, along with their tensile-strained counterparts, were systematically investigated as model systems. The thermodynamic and dynamic stability of these catalysts were confirmed through binding-energy analysis, COHP/ICOHP calculations, and vibrational frequency analysis. We comprehensively examined the adsorption and coupling behaviors of CO-derived intermediates and reveal that both metal identity and metal–metal distance strongly influence *CO adsorption, *OCCO adsorption, and C–C coupling energies. Volcano-type and monotonic relationships were identified, highlighting the synergistic roles of electronic structure and geometric configuration. To further elucidate the governing principles, we constructed interpretable machine-learning models using the sure independence screening and sparsifying operator (SISSE) algorithm²¹. Feature screening and descriptor selection identified the number of metal valence electrons and the metal–metal distance as the dominant factors controlling coupling energies. The resulting three-dimensional descriptor demonstrates reliable predictive performance and provides a practical framework for the rational design of DACs with enhanced C–C coupling activity.

2. Computational Details

DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP)²², employing the Generalized Gradient Approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional^{23–24}. A plane-wave energy cutoff of

450 eV and a $3 \times 3 \times 1$ Monkhorst-Pack grid for k-point sampling were set to ensure numerical precision. Convergence criteria were established at 10^{-5} eV for energy and 0.05 eV/Å for forces. Grimme's DFT-D3 dispersion correction was incorporated to account for long-range van der Waals interactions²⁵. Spin-polarization was applied throughout. A vacuum layer of 15 Å thickness was added in the z direction to avoid spurious interactions between periodic images. To reveal the interactions between metals and substrates, the crystal orbital Hamilton population (COHP) analysis was performed by LOBSTER package²⁶⁻²⁷.

The average binding energy (E_{ab}) was calculated by the following equation:

$$E_{ab} = (E_{M_2@NG} - E_{NG} - 2 \times E_M)/2$$

where $E_{M_2@NG}$ is the energy of the N-doped graphene substrate anchored with the two metal atoms. E_{NG} is the energy of the clean N-doped graphene substrate. E_M represents the energy of the isolated metal atom.

The average cohesive energy (E_{ac}) was calculated to represent the stability of different dual-atom metal, which is defined as the following equation:

$$E_{ac} = E_{bulk} - E_M$$

where E_{bulk} indicates the energy of the metal atom derived from the bulk crystal.

The adsorption energy for intermediates was calculated by

$$E_{ads} = (E_{ads+cat.} - E_{cat.} - n \times E_{ads})/n$$

where $E_{ads+cat.}$, $E_{cat.}$ and E_{ads} are the energies of catalysts with adsorbate, clean catalyst and adsorbate molecules, respectively. n is the number of adsorbate molecules.

The adsorption Gibbs free energy for molecule adsorption was calculated by the following equation:

$$\Delta G = E_{ads} + \Delta ZPE - T\Delta S$$

where E_{ads} is adsorption energy for intermediates, which obtained directly from DFT calculations, ΔZPE is the change of zero-point energies, T is the temperature of 298.15 K, and ΔS is the entropy change.

The commonly used sure independence screening and sparsifying operator (SISSO) algorithm was imported to train the integrated descriptors²¹. To obtain reasonable relationships between the integrated descriptors and catalytic performances (molecule adsorption energy and C–C coupling energy), the conventional mathematical operators are used in the formulation, including basic arithmetic (+, −, ×, /), logarithm, exponential, reciprocal, square, and square root functions. In SISSO, a large feature space is first constructed by iteratively combining primary physical features with a predefined set of mathematical operators. This procedure generates a vast number of candidate features. In the first step, the Sure Independence Screening (SIS) procedure evaluates the correlation between each candidate feature and the target property and retains the most relevant features. In the second step, the Sparsifying Operator (SO) identifies an optimal

low-dimensional descriptor by solving a sparse regression problem that minimizes the prediction error while limiting the number of selected features. The resulting model takes the form of an explicit analytical expression, which provides both predictive capability and physical interpretability.

3. Result and Discussion

We constructed 40 homonuclear (M–M) DACs with 3d transition metals and four different coordination structures (NG₁, NG₂, NG₃, and NG₄, Figure 1), denoted as M₂@NG_x (M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn). These coordination structures are classified according to the intermetallic distance between the two metal atoms. In the M₂@NG₁ and M₂@NG₂ configurations, the distance of metal atoms is relatively small, whereas in the M₂@NG₃ and M₂@NG₄ configurations, the distance is larger. To further investigate the influence of metal–metal distance on the coupling process, a 5% tensile strain was applied to each structure. After DFT structural optimization, the distances between most metal atoms were found to increase upon stretching (Figure S2). Moreover, the changes in interatomic distances for the M₂@NG₃ and M₂@NG₄ were larger than those for M₂@NG₁ and M₂@NG₂. This behavior likely arises because, in the M₂@NG₁ and M₂@NG₂ structures, the metal atoms are in close contact and exhibit strong metal–metal interactions. In addition, before stretching, the metal atoms deviate from the graphene plane, whereas after stretching they become nearly coplanar with the graphene support, especially for early transition metals (Sc, Ti, V) with large atomic radius (Figure S3-S7).

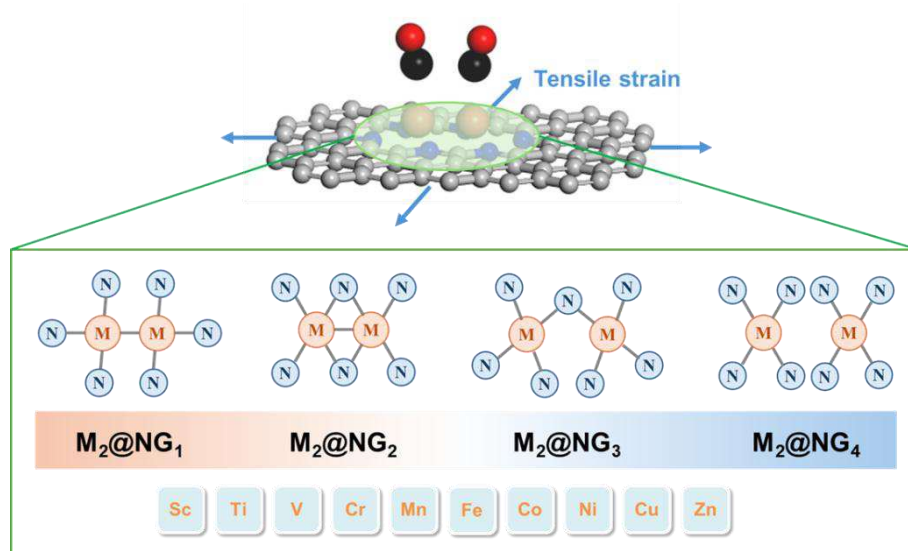


Figure 1. Schematic illustration of the dual-atom sites with transition metals in four coordination configurations (M₂@NG₁, M₂@NG₂, M₂@NG₃, and M₂@NG₄). Orange, blue, black and red spheres represent transition-metal atom, nitrogen atom, carbon atom and oxygen atom, respectively. The detailed structures are shown in Figure S1. Application of 5% tensile strain leads to different metal–metal interatomic distances.

For atomically dispersed catalysts, stability is of paramount importance. To evaluate the stability of $M_2@NG_x$ series, the differences between the average binding energies (E_{ab}) and the cohesive energies (E_{ac}) of DACs were calculated (Figure 2a and Figure S8). All values are negative, indicating that the DACs investigated in this work are thermodynamically stable. Further analysis revealed that for the $M_2@NG_2$ and $M_2@NG_3$ structures, tensile strain reduces stability. In contrast, for the $M_2@NG_1$ structures, stretching enhances the stability of the early transition metal while weakening that of the late transition metal, whereas the $M_2@NG_4$ structures exhibits opposite trend. This might be attributed to the shorter metal–metal distance in the $M_2@NG_1$ configuration: the larger atomic radius of the early transition metal induces intermetallic repulsion. Applying tensile strain weakens this repulsive interaction, thereby stabilizing the metal atoms. The binding strength of metal atoms on the substrate was further evaluated using the crystal orbital Hamiltonian population (COHP) (Figure S10-S14) and integrated crystal orbital Hamilton populations (ICOHPs) between metal atom and coordination N atom (Figure 2b and Figure S9). After applying tensile strain, the COHP peaks near the Fermi level decrease for all metals except Zn, and the corresponding ICOHP magnitudes are reduced, indicating weakened metal–support interactions upon stretching. Moreover, the vibrational frequencies of the dual-atom sites were performed using the finite-difference method. Six vibrational modes were obtained for the two metal atoms, corresponding to their three-dimensional motions. For all $M_2@NG_x$ configurations, all frequencies are positive, confirming their dynamic stabilities of the M_2 active sites (Table S1-S10). Based on these analyses, although tensile strain may slightly reduce the stability of certain diatomic catalysts, the $M_2@NG_x$ structures considered in this work are, overall, sufficiently stable.

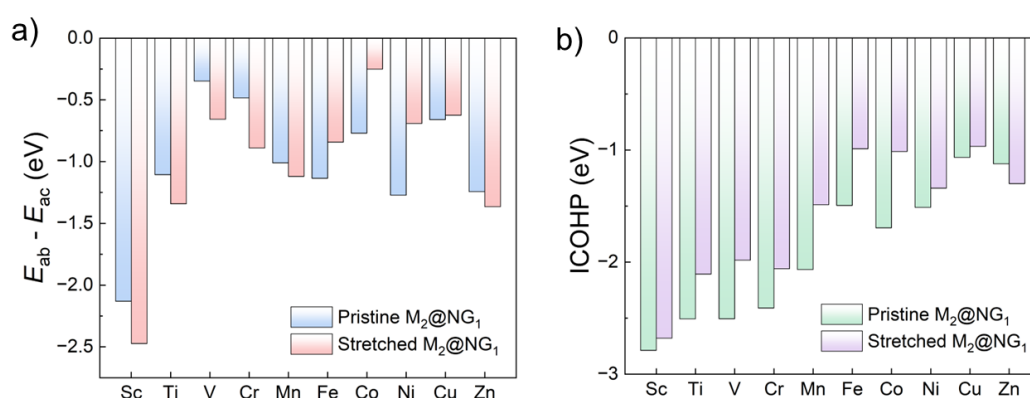


Figure 2. a) Differences between the average binding energies (E_{ab}) and the cohesive energies (E_{ac}) of $M_2@NG_1$. b) IpCOHPs values for the M–N bond in $M_2@NG_1$.

*CO has been identified as the key intermediate during CO_2RR and plays a crucial role in the formation of multi-carbon products²⁸⁻²⁹. Accordingly, the CO coupling ($*CO + *CO \rightarrow *OCCO$) constitutes a critical step in the formation of C_2 species. Therefore, understanding

how metal properties influence the adsorption of reactant and product intermediates is of great importance. Herein, we investigated the adsorption behavior of CO and OCCO on $M_2@NG_x$ catalysts. For CO adsorption, previous studies have demonstrated that the catalytically active sites of $M_2@NG_x$ are the metal atoms rather than C or N sites³⁰. The top-bridged and top-top configurations are the most probable adsorption modes for two CO molecules on DACs³¹⁻³². The calculated adsorption free energies (ΔG_{2^*CO}) of two CO molecules on $M_2@NG_x$ are shown in Figure 3a and Figure S15. For small metal-metal distance (e.g., pristine $M_2@NG_1$), top-bridged configurations are more exothermic than top-top configurations, particularly for early transition metals (e.g., Sc, Ti, V and Cr). After applying tensile strain, the top-top configurations for $Co_2@NG_1$ and $Cu_2@NG_1$ become thermodynamically more stable. For catalysts with larger metal-metal distance ($M_2@NG_2$, $M_2@NG_3$ and $M_2@NG_4$), most adsorption structures favor the top-top configuration, especially for the stretched systems. Previous reports indicate that the optimal CO adsorption energy for CO₂RR is approximately -0.5 eV per molecule³³. Excessively strong CO binding hinders product desorption, such that C-C coupling is no longer the rate-determining step. Compared with early transition metals, which bind CO strongly, later metals (e.g., Ni and Cu) exhibit more moderate CO adsorption. We further compared the most stable adsorption energies of two CO molecules for pristine $M_2@NG_x$ and stretched $M_2@NG_x$ (Figure 3b and Figure S16). As the atomic number increases, the CO adsorption strength shows an overall increasing trend. Moreover, tensile strain weakens CO adsorption on early transition metals, whereas it enhances CO adsorption on later transition metals, with Fe or Co marking the boundary between weakening and enhancement.

For OCCO adsorption, probable configurations on DACs can be classified as single-site and dual-site modes. The calculated adsorption free energies (ΔG_{OCCO}) are presented in Figure 3c and Figure S17. For most metals in $M_2@NG_1$, $M_2@NG_2$ and $M_2@NG_3$, dual-site configurations are more exothermic than single-site ones and remain favored after stretching. Notably, when the metal-metal distance becomes relatively large (e.g., stretching $M_2@NG_3$), OCCO still adopts a dual-site geometry, but the dominant bonding mode changes from C-M to O-M. With a further increase in distance ($M_2@NG_4$), latter transition metals (e.g. Cr, Mn, Fe, Co, and Cu) preferentially exhibit single-site adsorption. We also compared the most stable adsorption energies of $^*OCCO$ on pristine and stretched $M_2@NG_x$ (Figure 3d and Figure S18). Similar to CO adsorption, the adsorption strength increases with atomic number. Tensile strain weakens OCCO adsorption on early transition metals but enhances it on later transition metals, again with Fe or Co defining the boundary. And the boundary between enhancement and weakening is the Fe or Co metal. These results demonstrate that both metal-metal distance and electronic properties of active centers strongly govern the adsorption configuration and energetics of key C-C coupling

intermediates.

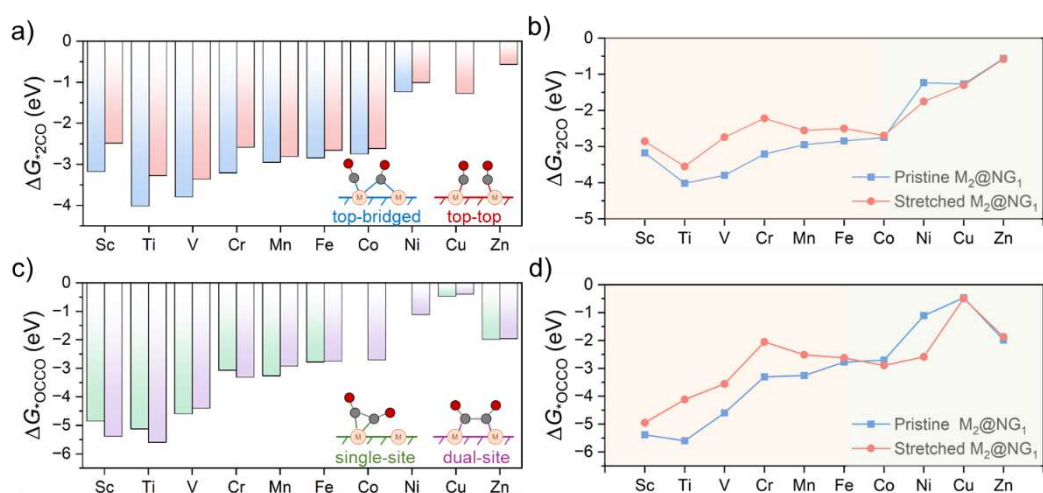


Figure 3. a) Adsorption energies of two CO molecules on pristine $M_2@NG_1$ in top-bridged (blue bars) and top-top (red bars) configurations, the illustration in figure represents the top-bridged and top-top configurations of two CO molecules on the DAC. b) Comparison of the most stable adsorption energies of two CO molecules on pristine $M_2@NG_1$ and stretched $M_2@NG_1$. c) Adsorption energies of $^*OCCO$ molecules on $M_2@NG_1$ in single-site (green bars) and dual-site (purple bars) configurations, the illustration in figure represents the single-site and dual-site configurations of $^*OCCO$ molecules on the DAC. d) Comparison of the most stable adsorption energies of $^*OCCO$ molecules on pristine $M_2@NG_1$ and stretched $M_2@NG_1$.

Because different metals possess distinct physicochemical properties, clarifying their influence on the C–C coupling process is essential for rational catalyst design. Accordingly, we investigated the effects of metal identity and interatomic distance on adsorption and coupling behaviors. For CO adsorption, the adsorption free energy exhibits an inverse volcano-type trend with increasing atomic number, first decreasing and then increasing (Figure 4a and Figure S19). Across different NG supports, the metals corresponding to the minimum adsorption energy are Ti or V. In contrast, the relationship between adsorption energy and metal–metal distance follows a volcano-type trend: CO adsorption initially weakens and then strengthens as the interatomic distance increases, with the optimal distance for the weakest adsorption varying among different metals (Figure 4c and Figure S20). For $^*OCCO$ adsorption, unlike CO, the adsorption strength decreases monotonically with increasing atomic number (Figure 4b and Figure S21). However, there is only a weak inverse volcanic relationship between adsorption and metal–metal distance. (Figure 4d and Figure S22). We further evaluated the coupling energy, defined as the energy difference between $^*OCCO$ and $^*2CO$ adsorption. The results show that the coupling energy also follows an inverse volcano-type trend with respect to atomic number (Figure 5a and Figure S23), while exhibiting no obvious correlation with metal–metal distance

(Figure 5b and Figure S24). Therefore, although the electronic and geometric properties of metal centers are key factors governing the C–C coupling process, the specific principles that dictate intermediate adsorption and coupling behavior remain unclear.

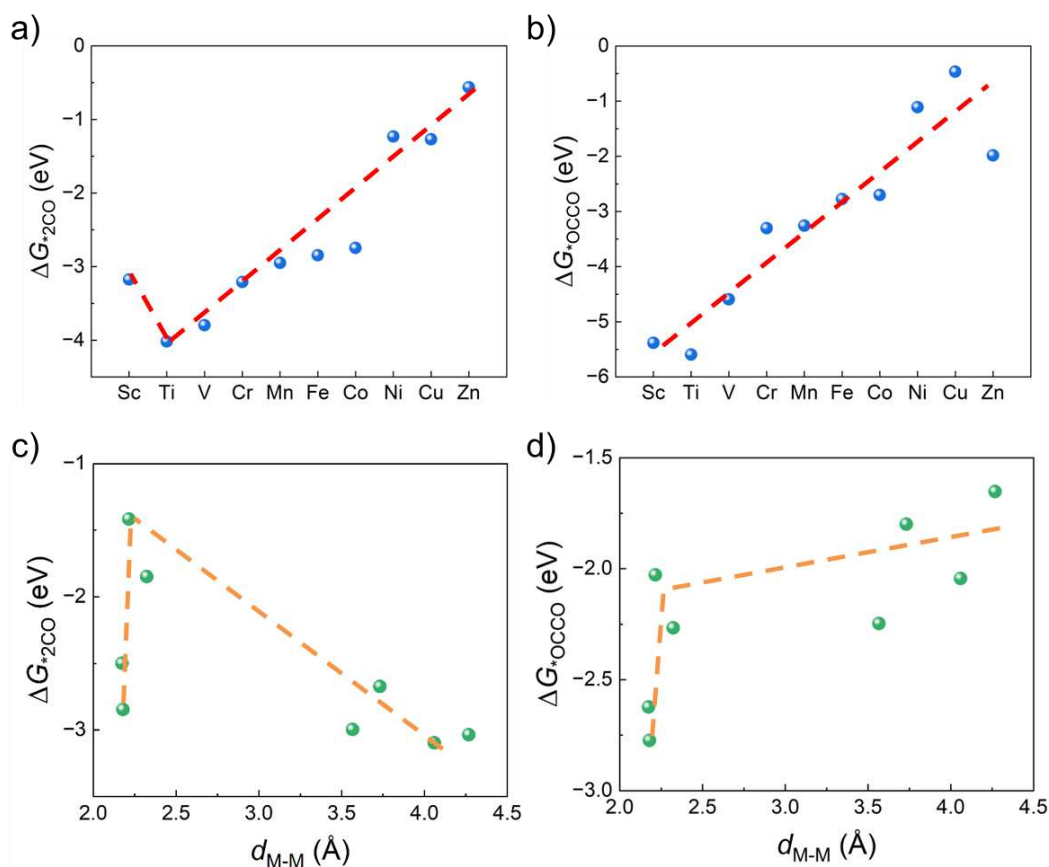


Figure 4. Adsorption energies of a) two CO molecules and b) *OCCO molecules as a function of metal identity in $M_2@NG_1$. Adsorption energies of c) two CO molecules and d) *OCCO molecules as a function of metal–metal distance in $Fe_2@NG_x$.

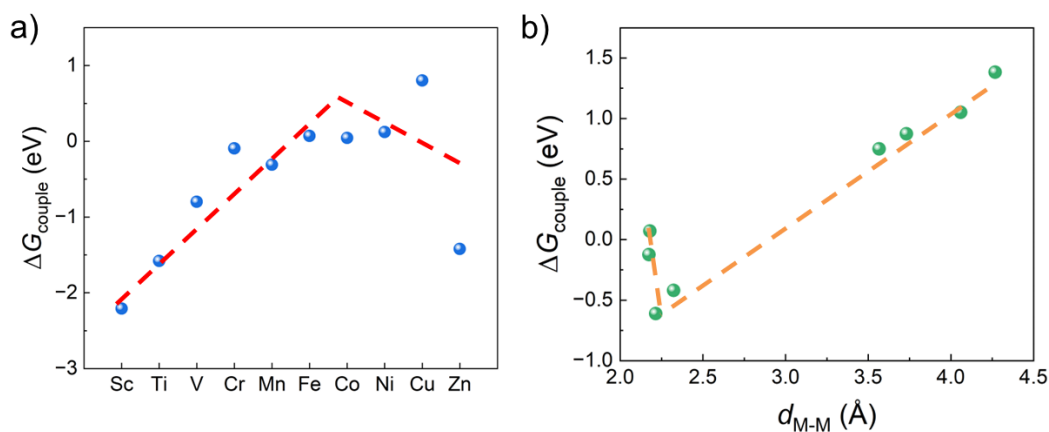


Figure 5. a) C–C coupling energies as a function of metal identity in $M_2@NG_1$. b) C–C coupling energies as a function of metal–metal distance in $Fe_2@NG_x$.

To further elucidate the correlation between C–C coupling process and catalyst properties, machine learning (ML) provides an effective framework. Features selection is critical for training reliable ML models. Selected features should be unique, computationally inexpensive or readily available from public databases, and, most importantly, capable of directly reflecting the physicochemical properties of catalytic materials to ensure both accuracy and interpretability of the predictions. Based on these criteria, sixteen features were selected and classified into three groups (electronic-structure-based, geometric, and general parameters), as summarized in Table S11. Although incorporating more features may improve predictive accuracy, it often leads to reduced training efficiency and increased risk of overfitting. To mitigate this issue, the Pearson correlation coefficient (PCC) was employed to quantify pairwise correlation among features, followed by feature screening to eliminate redundancy. As shown in Figure 6a and Figure S25, the feature set was reduced from sixteen to eight by ensuring that the absolute PCC between any two descriptors remained below 0.8. In the PCC heatmap, darker colors indicate stronger correlations. Some descriptors inevitably exhibit moderate correlation because physicochemical properties are intrinsically interconnected.

Understanding feature importance is essential not only for accurate prediction but also for revealing the underlying physicochemical principles governing catalytic behavior. The SHapley Additive exPlanations (SHAP) algorithm³⁴ was used to evaluate the contributions of the eight retained descriptors (Figure 6b). The four most influential features are the number of metal valence electrons (N_M^{VE}), the metal–metal distance (d_{MM}), the covalent radius of the metal (R_M^{CR}), and the Pauling electronegativity (χ_M). This ranking indicates that model performance is primarily controlled by descriptors associated with the electronic and geometric properties of the metal centers, consistent with the DFT trends shown in Figure 4 and Figure 5. To further improve model robustness, regularization was applied after feature reduction to identify potential anomalies. The normalized distributions of all descriptors are shown in Figure S26, with values ranging from –2 to +3, confirming that the selected descriptors are physically reasonable and free of significant outliers.

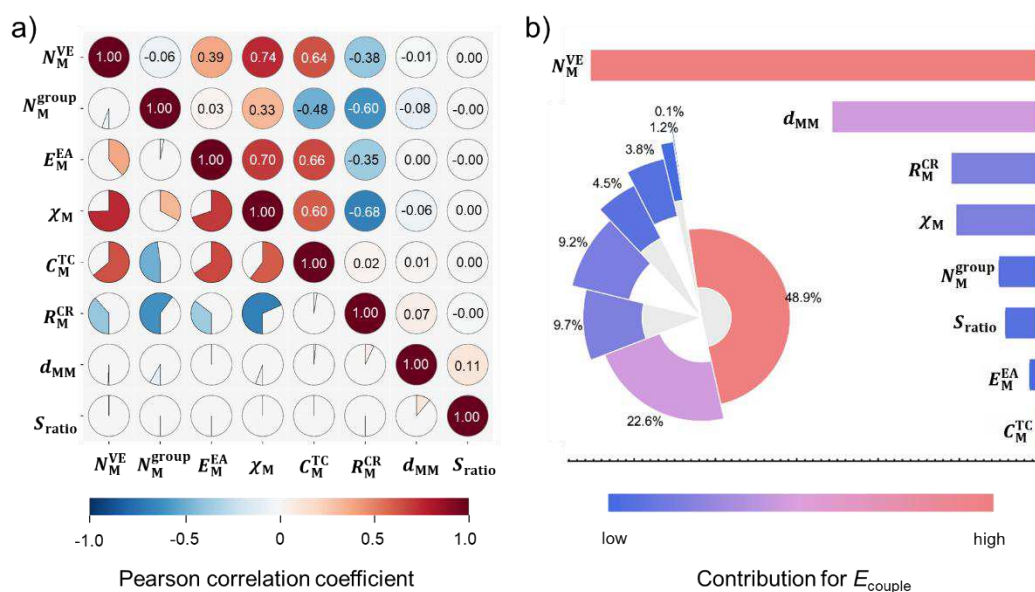


Figure 6. a) Pearson correlation coefficients among screened features. b) Feature-importance ranking obtained using the SHAP method.

After feature selection, we employed the interpretable machine-learning method SISSO to identify key descriptors and construct a quantitative descriptor formula. Compared with other interpretable models such as linear regression, least absolute shrinkage and selection operator (LASSO) regression, or decision-tree-based methods, SISSO offers several advantages. First, SISSO is particularly suitable for small datasets typical of first-principles calculations, where the number of samples is limited but the potential descriptor space is extremely large. Second, SISSO systematically explores a vast feature space and can identify non-linear combinations of physically meaningful variables, enabling the discovery of compact analytical expressions that capture the key factors governing catalytic activity. In contrast, conventional linear models are restricted to predefined features and may fail to capture complex relationships, while tree-based models often lack clear analytical expressions. Therefore, SISSO provides a powerful and interpretable framework for identifying fundamental descriptors that govern catalytic performance, and has shown strong performance in materials property prediction³⁵⁻³⁶. In this study, SISSO can efficiently screen relevant features from a high-dimensional space, thereby reducing computational cost and accelerating descriptor optimization. Moreover, it can identify physically interpretable descriptors that link catalytic performance to underlying electronic and geometric properties, which is particularly valuable for understanding activity trends in dual-atom catalysts.

The initial descriptor pool comprised the eight selected features, which were treated as potential variables governing the coupling energy. To balance predictive accuracy and efficiency, we evaluated SISSO models of different dimensionalities (Figure 7a). Increasing dimensionality decreases the root-mean-square error (RMSE) and increases the

coefficient of determination (R^2); however, the improvement becomes marginal beyond three dimensions. Therefore, a three-dimensional descriptor was selected to ensure both accuracy and computational efficiency. The predictive performance of the ML model for coupling energy is presented in Figure 7b, yielding an RMSE of 0.31 eV. The resulting descriptor formula incorporates features such as the number of metal valence electrons and the metal–metal distance (Figure 7c), in agreement with the DFT analysis and SHAP results. This agreement indicates that the electronic and geometric properties of the metal centers are the key factors governing the C–C coupling process. This consistency confirms that the electronic and geometric properties of metal centers govern the C–C coupling process. By applying the derived descriptor, computational cost can be substantially reduced, enabling rapid screening of potential catalysts for C₂ product formation.

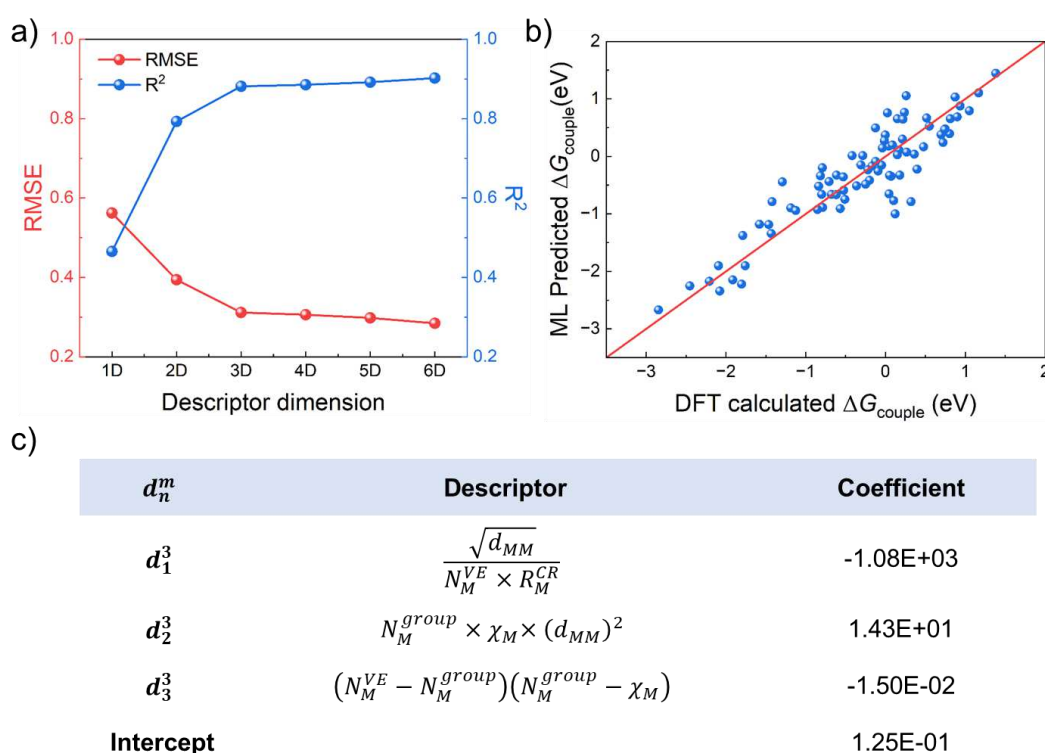


Figure 7. a) Training RMSE and R^2 for SISSO models with different hyperparameter settings. b) Comparison between machine-learning predictions and DFT-calculated C–C coupling energies (ΔG_{couple}). c) Identified descriptors and their corresponding coefficients in the SISSO models.

4. Conclusion

In this work, we combine density functional theory (DFT) with interpretable machine learning to investigate fourth-row transition-metal dual-atom catalysts ($M_2@NG_x$) and elucidate how geometric and electronic factors synergistically regulate the C–C coupling process. By examining eighty DAC structures with multiple coordination environments, we confirm that all catalysts exhibit good thermodynamic and dynamic stability, as evidenced

by binding-energy analysis, COHP/ICOHP calculations, and vibrational frequency analysis. Our results show that the adsorption and coupling behaviors of CO-derived intermediates strongly depend on both the metal identity and the metal–metal distance. The adsorption of *CO and *OCCO displays distinct trends with respect to atomic number and interatomic distance, giving rise to volcano-type or monotonic relationships. Importantly, the C–C coupling energy exhibits a volcano-type dependence on the metal species, whereas its relationship with metal–metal distance varies across different metals. This behavior highlights the critical synergy between the geometric configuration and electronic structure of the active sites. To reduce computational cost and accelerate catalyst discovery, we further developed interpretable SISO-based machine-learning models using physically meaningful features. Feature screening via Pearson correlation analysis, SHAP importance ranking, and SISO selection identifies the number of metal valence electrons and the metal–metal distance as the dominant factors governing coupling energies. The final SISO-derived three-dimensional descriptor achieves good predictive performance with an RMSE of 0.31 eV, enabling reliable prediction of C–C coupling performance for catalyst candidates. Overall, this work clarifies the fundamental principles by which dual-atom geometry and electronic properties control C–C coupling in CO₂RR. The combined DFT–ML framework provides an efficient and reliable strategy for the rational design of dual-atom catalysts capable of promoting C₂ product formation.

Supporting Information

Metal–metal distance, differences between the average binding energies (E_{ab}) and the cohesive energies (E_{ac}), vibrational frequencies, I_p COHPs values, COHP curves, adsorption energies of two CO molecules and *OCCO molecules, C–C coupling energies, primary features, and pearson correlation coefficients (PDF).

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Author contributions

Chenglong Qiu and Jiacheng Wang conceived and designed the research. Chenglong Qiu performed the calculations and analyzed the data. Chenglong Qiu wrote the original draft of the manuscript. Chenglong Qiu, Tore Brinck and Jiacheng Wang reviewed and revised the manuscript.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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