

Dual-metal synergy in electrocatalytic urea synthesis: mechanistic study of Fe-doped $W_{18}O_{49}(010)$ for CO_2 and NO_3^- coupling

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The electrocatalytic co-reduction of carbon dioxide (CO_2) and nitrate (NO_3^-) to urea represents a promising dual-purpose strategy, offering a sustainable alternative to the energy-intensive Bosch-Meiser process while simultaneously mitigating environmental pollutants. This study systematically explores the catalytic performance of a series of transition-metal-doped $W_{18}O_{49}(010)$ surfaces (TM- $W_{18}O_{49}$, TM = Fe, Co, Ni, Cu, Zn) for urea synthesis using first-principles calculations. Among them, Fe-doped $W_{18}O_{49}$ emerges as the most promising electrocatalyst, exhibiting superior activity with a remarkably low limiting potential of -0.46 V (compared to -0.95 V for pristine $W_{18}O_{49}$) and outstanding selectivity by effectively suppressing competing nitrate reduction and hydrogen evolution reactions. Mechanistic analysis reveals a heteronuclear dual-metal (TM-W) synergistic adsorption mechanism, in which the doped transition metal and adjacent W site collaboratively activate NO_3^- , thereby facilitating the critical C–N bond formation. This work not only elucidates the reaction pathway and active-site synergy in Fe- $W_{18}O_{49}$, but also provides a theoretical foundation for the rational design of high-performance bimetallic oxide catalysts towards efficient electrocatalytic urea production.

urea electrosynthesis; dual-metal synergy; heteronuclear doping; C–N coupling

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1. Introduction

Urea (NH_2CONH_2), as an important nitrogen fertilizer, plays a significant role in agriculture yields.^[1–2] Currently, industrial urea manufacturing largely relies on ammonia (NH_3) synthesized *via* the Haber-Bosch process, which reacts with carbon dioxide (CO_2) under high temperature and high pressure (150 to 200 °C, 15 to 25 MPa). This conventional route not only consumes substantial energy but also emits significant amounts of CO_2 , highlighting an urgent need for more sustainable alternatives.^[3–6] Electrocatalytic urea synthesis from N_2 and CO_2 has emerged as an attractive green strategy, yet its practical implementation remains challenging due to the inherent inertness of $N\equiv N$ triple bond (941 $kJ\cdot mol^{-1}$) and the low solubility of N_2 in aqueous electrolytes.^[7–8] In recent years, nitrate (NO_3^-) has gained attention as a more reactive and soluble nitrogen source for electrocatalytic C–N coupling, owing to its lower N–O bond dissociation energy (204 $kJ\cdot mol^{-1}$) and higher

solubility.^[9–12] This shift has spurred extensive research into transition metal oxide catalysts for co-reduction of NO_3^- and CO_2 to urea.

For instance, Zn single atoms anchored on oxygen-deficient In_2O_{3-x} surface have been demonstrated to activate NO_3^- efficiently, forming $*NH_2$ intermediates, while the oxygen vacancies promote CO_2 activation to generate $*CO$ species, thereby synergistically enhancing urea synthesis.^[13] Similarly, MoO_x nanoclusters supported on carbon black, which possess abundant unsaturated sites, effectively modulate the adsorption and activation of key intermediates throughout the urea synthesis pathway.^[14] In another system comprising amorphous Fe and Fe_3O_4 nanoparticles loaded on carbon nanotubes, Fe sites facilitate the reduction of NO_3^- to $*NH_2$ intermediates, while Fe_3O_4 promote CO_2 conversion to $*CO$ intermediates, achieving cooperative catalysis for high-efficiency urea production.^[15] Furthermore, in Cu/ Cu_2O heterostructures applied in urea desorption, the introduction of Cu mitigates the inhibitory effect of Cu_2O on urea desorption, leading to a significant increase in urea yield.^[16] These studies collectively indicate that single-component transition metal oxides often exhibit

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limited catalytic efficiency for urea synthesis, whereas heteronuclear systems can substantially enhance performance through synergistic interactions. Further investigations have highlighted the role of oxygen vacancies as additional active sites. For example, oxygen vacancy-rich V_O - $\text{In}(\text{OH})_3$ modifies the adsorption configuration of C—N coupling intermediates on In sites, achieving a Faradaic efficiency of 80.1% for urea synthesis.^[17] In V_O - In - TiO_2 system, oxygen vacancies serve as direct active sites, efficiently catalyzing the reduction of NO_3^- to $^*\text{NH}_2$ intermediates and thereby laying the foundation for subsequent C—N coupling.^[18] $\text{W}_{18}\text{O}_{49}$, a representative transition metal oxide, has attracted considerable attention in catalysis due to its distinctive structural features, including abundant intrinsic oxygen vacancies and extensive tunnel-like cavities within its crystalline framework.^[19–23] Our previous studies have demonstrated that Cu-doped $\text{W}_{18}\text{O}_{49}$ enhances urea synthesis from CO_2 and NO_3^- by electronic modulation of adjacent W sites.^[24] Furthermore, we extended this doping strategy to explore transition metal (TM = Fe, Co, Ni) doping on the $\text{W}_{18}\text{O}_{49}(\bar{1}01)$ facet for urea synthesis from CO_2 and N_2 by creating distinct adsorption sites, mitigating reactant competition.^[25]

Building upon these findings, the current study investigates a series of 3d transition metal (TM = Fe, Co, Ni, Cu, Zn) doped $\text{W}_{18}\text{O}_{49}(010)$ surface (TM- $\text{W}_{18}\text{O}_{49}$) through first-principles calculations. By harnessing the abundant intrinsic oxygen vacancies of $\text{W}_{18}\text{O}_{49}$ and the electronic modulation introduced by heterometallic doping, we aim to achieve enhanced catalytic activity and selectivity for urea production. Our computational results demonstrate that the incorporation of TM dopants not only tunes the electronic structure of the host oxide but also creates a heteronuclear dual-metal (TM-W) synergy that collaboratively activates NO_3^- and facilitates C—N bond formation. In particular, the Fe-doped $\text{W}_{18}\text{O}_{49}$ system exhibits exceptional performance, with a significantly reduced limiting potential and effective suppression of competing side reactions. This study elucidates the detailed reaction pathway and the role of TM-W synergy in urea formation, offering theoretical guidance for the rational design of efficient bimetallic oxide electrocatalysts.

2. Computational methods

All density functional theory (DFT) calculations were performed using the Vienna Ab Initio Simulation Package (VASP 5.4.1).^[26] The exchange-correlation energy was treated with the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).^[27–28] The projector augmented wave (PAW) method was employed to describe the interactions between atoms and electrons,^[29] while van der Waals interactions were accounted for using the DFT-D3 correction.^[30] A 1.5 nm vacuum layer was added along the perpendicular direction to avoid interlayer interactions. A plane-wave energy cutoff of

500 eV was applied for the basis set expansion. During structural optimization and frequency calculations, the bottom two atomic layers were fixed, with force and energy convergence thresholds set to $0.5 \text{ eV}\cdot\text{nm}^{-1}$ and 10^{-5} eV , respectively. A Monkhorst Pack ($2 \times 2 \times 1$) Brillouin zone k -point mesh centered on Gamma was used.

The formation energy (E_f) of the TM-doped $\text{W}_{18}\text{O}_{49}$ system is defined as:

$$E_f = E_{\text{TM-}\text{W}_{18}\text{O}_{49}} + E_{\text{W}} - E_{\text{W}_{18}\text{O}_{49}} - E_{\text{TM}}, \quad (1)$$

where $E_{\text{TM-}\text{W}_{18}\text{O}_{49}}$ and $E_{\text{W}_{18}\text{O}_{49}}$ represent the total energies of the TM-doped $\text{W}_{18}\text{O}_{49}$ system and pristine $\text{W}_{18}\text{O}_{49}$ system, respectively, while E_{W} and E_{TM} denote the energies of an isolated W atom and the dopant transition metal (TM) atom in their reference states.

The catalytic performance of TM- $\text{W}_{18}\text{O}_{49}$ for urea synthesis from inert NO_3^- and CO_2 was evaluated by calculating the ΔG at zero applied potential and pH = 0 using the computational hydrogen electrode (CHE) model.^[31–33]

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S, \quad (2)$$

where ΔE_{ZPE} and ΔS represent the differences in zero-point energy and entropy, respectively, between the adsorbed species and gas-phase molecules, as calculated from vibrational frequency analysis; T denotes the temperature of 298.15 K.

The limiting potential (U_L) is to describe electrocatalytic activity, which has been defined as:

$$U_L = -\Delta G_{\text{max}} / e, \quad (3)$$

where ΔG_{max} is the Gibbs free energy change of the potential determining step (PDS).

3. Results and discussion

3.1 Structure and stability of TM- $\text{W}_{18}\text{O}_{49}$ (TM=Fe, Co, Ni, Cu, Zn)

Previous studies have demonstrated that Co-, Ni-, Cu- and Zn-doped $\text{WO}_{2.7-x}$ can be successfully synthesized *via* vacancy engineering and transition metal doping for various application.^[20,24–25,34–35] Based on these reports, we constructed a $1 \times 1 \times 2$ supercell of pristine $\text{W}_{18}\text{O}_{49}$ with the (010) facet as the active surface. The supercell parameters are $a = 1.784 \text{ nm}$, $b = 1.413 \text{ nm}$, $c = 2.072 \text{ nm}$, $\alpha = \beta = 90^\circ$, and $\gamma = 110.53^\circ$ with a W/O atomic ratio of approximately 1/2.7. Transition metals from the latter half of the 3d series (Fe, Co, Ni, Cu, Zn) were selected as dopants, based on two key considerations: (a) their smaller atomic radii relative to W, which facilitates substitutional doping; (b) their varied d-electron configurations, which enable effective modulation of the electronic structure of $\text{W}_{18}\text{O}_{49}$. Two potential substitution sites on the (010) surface, denoted as TM-a and TM-b (See Figure 1a), were systematically evaluated by replacing a single W atom with each of the five transition metals, yielding the corresponding TM- $\text{W}_{18}\text{O}_{49}(010)$ surface models. The formation energies of these doped systems were calculated to assess their structural stability (See Fig-

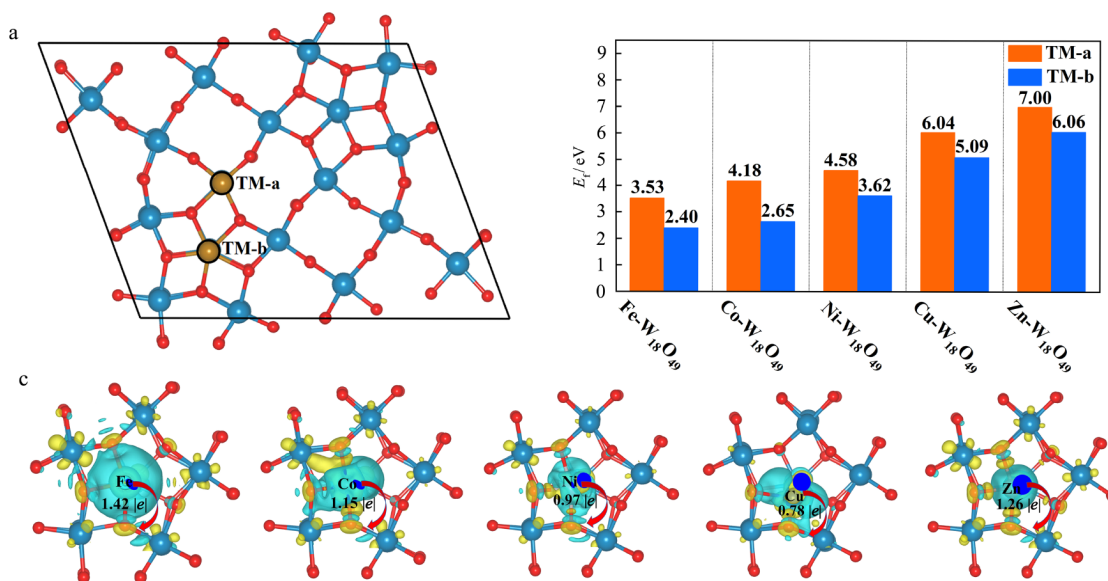


Figure 1 Two possible substitution sites for metal doping on the W₁₈O₄₉(010) surface (a), calculated E_f of TM-W₁₈O₄₉ at two doping sites (b), and charge density difference (iso-surface value is $2\ e\text{-nm}^{-3}$) and corresponding charge transfer between dopant TM atoms and the W₁₈O₄₉ matrix (c)

ure 1b). The results indicate that doping at the TM-b site leads to higher formation energies (2.40, 2.65, 3.62, 5.09, and 6.06 eV for Fe, Co, Ni, Cu, and Zn, respectively), demonstrating that this site provides superior stability for the doped structures.

To further elucidate the interaction between the dopant atoms and the W₁₈O₄₉ host, Bader charge analysis was performed. The calculated charge transfers from the TM atoms to the W₁₈O₄₉ host are 1.42| e | for Fe-W₁₈O₄₉, 1.15| e | for Co-W₁₈O₄₉, 0.97| e | for Ni-W₁₈O₄₉, 0.78| e | for Cu-W₁₈O₄₉, and 1.26| e | for Zn-W₁₈O₄₉, respectively. Charge density difference plots (See Figure 1c) further reveal significant electron depletion (cyan regions) around the dopant atoms and electron accumulation (yellow regions) on adjacent oxygen atoms, confirming strong electronic coupling between the dopants and the host lattice. A linear correlation ($R^2 = 0.86$) is observed between the formation energy and the Bader charge transfer for the Fe-, Co-, Ni- and Cu-doped systems (See Figure 2), suggesting that greater charge transfer generally corresponds to higher structural stability. The distinct behavior of Zn may be attributed not only to its lower electronegativity (Zn: 1.65, Fe: 1.83, Co: 1.88, Ni: 1.91, Cu: 1.90) but also to a more ionic character in its bonding with oxygen atoms in the W₁₈O₄₉ matrix, as suggested by its larger charge transfer and deviation from the linear trend observed for Fe, Co, Ni and Cu. Overall, the calculated formation energies and charge-transfer characteristics confirm the structural stability and strong dopant-host interactions in the TM-W₁₈O₄₉ systems, providing a solid foundation for their subsequent evaluation as electrocatalysts for urea synthesis.

3.2 Adsorption of NO₃[−] on TM-W₁₈O₄₉

Effective adsorption and activation of NO₃[−] are critical in-

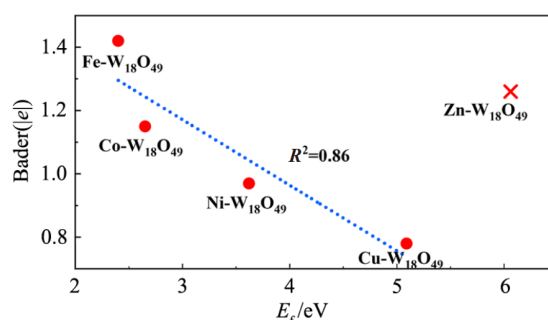


Figure 2 Linear correlation between formation energy and Bader charge transfer in TM-W₁₈O₄₉ doped systems

itial steps for electrocatalytic urea synthesis from NO₃[−] and CO₂.^[36–38] To evaluate the role of transition metal doping in this process, we systematically investigated the adsorption behavior of NO₃[−] on the (010) surface of TM-W₁₈O₄₉ (TM = Fe, Co, Ni, Cu, Zn). Six distinct adsorption configurations were considered, including adsorption on pure W-W sites and five different TM-W dual-metal sites (See Figure 3). The calculated adsorption energies (E_{ads}) reveal distinct trends across the doped systems. For Fe-, Co-, Ni- and Zn-W₁₈O₄₉, NO₃[−] preferentially adsorbs at the heteronuclear TM-W dual-metal sites, with E_{ads} values ranging from -3.02 to -3.44 eV (See Figure 4). These results indicate that in most TM-W doped systems, the introduced transition metal atoms actively participate in NO₃[−] adsorption, serving not merely as electronic modulators but rather as integral components of the active site.^[19,39]

The strong adsorption of NO₃[−] at TM-W sites can be attributed to the synergistic electronic interaction between the dopant TM and adjacent W atoms, which enhances charge transfer to the NO₃[−] and facilitates its activation. Notably, Fe-W₁₈O₄₉ exhibits the strongest NO₃[−] adsorption ($E_{\text{ads}} = -3.44$ eV), consistent with its previously discussed

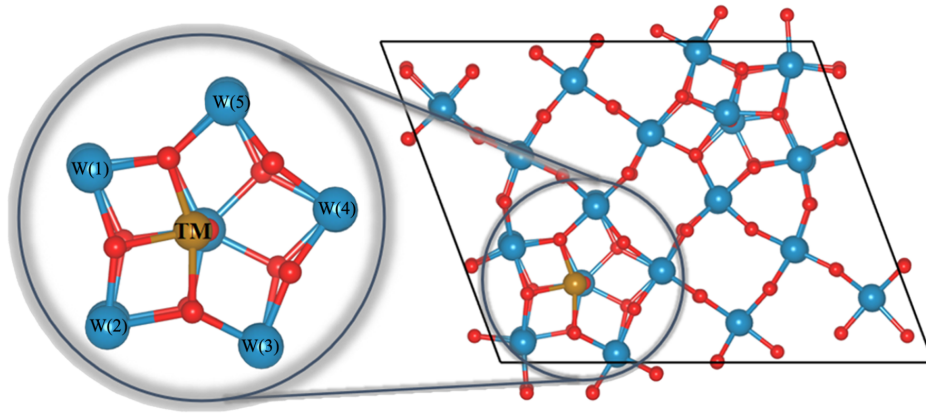
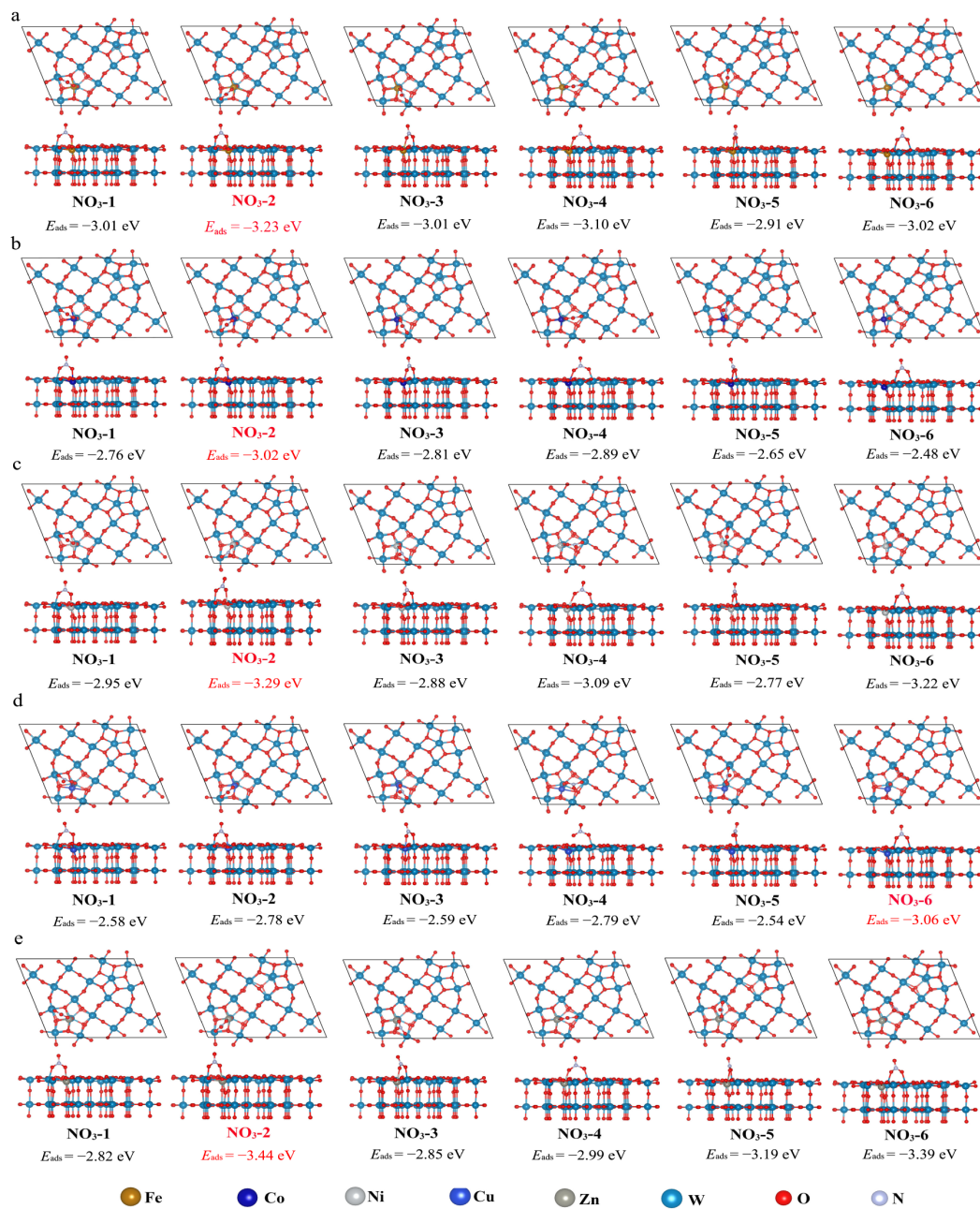


Figure 3 Possible doped sites of transition metal and the corresponding different W sites on TM- $W_{18}O_{49}(010)$ surface



The lowest E_{ads} value is marked in red

Figure 4 Six distinct adsorption configurations of NO_3^- on Fe- $W_{18}O_{49}$ (a), Co- $W_{18}O_{49}$ (b), Ni- $W_{18}O_{49}$ (c), Cu- $W_{18}O_{49}$ (d), Zn- $W_{18}O_{49}$ (e), and their corresponding adsorption energies (E_{ads})

high charge transfer and structural stability. The exceptional behavior of Zn-W₁₈O₄₉ may stem from the unique electronic structure of Zn, which favors adsorption at W-rich sites under the studied surface configuration. These findings underscore that transition metal doping not only tailors the electronic properties of W₁₈O₄₉ but also creates hetero-nuclear active sites that enhance NO₃[−] adsorption, a crucial prerequisite for its subsequent reduction and coupling with CO₂ in the urea synthesis pathway.

3.3 Catalytic activity of TM-W₁₈O₄₉ toward urea production

Previous studies have suggested that C–N bond formation in urea synthesis may occur *via* coupling between *CO (from CO₂ reduction) and *NO (from NO₃[−] reduction), with supporting evidence from infrared signals of the *OCNO intermediate.^[40] However, the use of *CO as a carbon precursor faces intrinsic limitations, including sluggish desorption kinetics and a tendency toward over-reduction, which can lead to diverse byproducts and hinder efficient C–N coupling.^[41–42] To overcome these challenges, we propose a direct C–N coupling mechanism between CO₂ and *NO, motivated by favorable orbital alignment between the highest occupied molecular orbital (HOMO) of CO₂ and the

lowest unoccupied molecular orbital (LUMO) of *NO intermediates. As illustrated in Figure 5a, the proposed reaction pathway initiates with the direct coupling of CO₂ with adsorbed *NO to form *NOCO₂, followed by successive hydrogenation steps leading to the key intermediate *NOCO. Subsequent hydrogenation yield *NH₂CO, which then undergoes a second C–N coupling with another *NO to form *NH₂CONO. Further hydrogenation ultimately produces NH₂CONH₂.

The Gibbs free energy diagrams for urea synthesis on TM-W₁₈O₄₉ (TM = Fe, Co, Ni, Cu, Zn) surfaces are presented in Figures 5b–5f, with the optimized structures of key intermediates on Fe-W₁₈O₄₉ surface shown in Figure 6. The reaction begins with NO₃[−] adsorption, which is strongly exothermic on all doped surfaces ($E_{\text{ads}} < -3.00$ eV). Taking Fe-W₁₈O₄₉ as a representative system, NO₃[−] preferentially adsorbs at the Fe-W2 dual-metal site, highlighting the synergistic role of the dopant and W atoms in nitrate activation. The adsorbed NO₃[−] undergoes stepwise hydrogenation to form *NO₂ ($\Delta G = -1.99$ eV) and subsequently *NO ($\Delta G = 0.13$ eV), confirming the thermodynamic feasibility of *NO generation as a key nitrogen precursor. On Fe-W₁₈O₄₉, the first C–N coupling proceeds through a direct interaction between the adsorbed *NO intermediate and gaseous CO₂ to form *NOCO₂, a step that is exothermic with $\Delta G = -0.46$ eV.

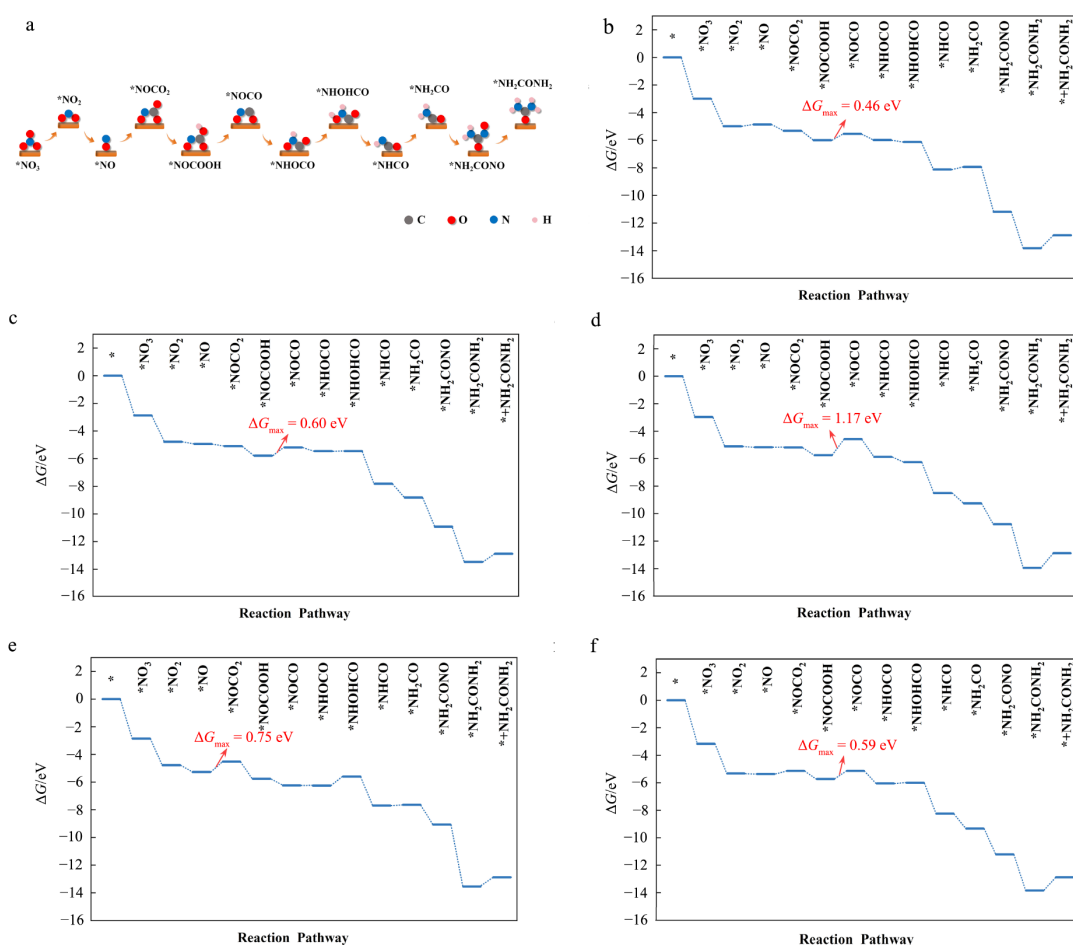


Figure 5 Proposed reaction mechanism for the electrochemical synthesis of urea from NO₃[−] and CO₂ catalyzed by TM-W₁₈O₄₉ surfaces (a), and calculated Gibbs free energy diagrams for urea production on TM-W₁₈O₄₉ (TM = Fe, Co, Ni, Cu, Zn) (b–f)

This direct coupling mechanism aligns with previously reported pathways involving $^*\text{NO}$ and CO_2 .^[41,43] Subsequent hydrogenation to $^*\text{NOCO}^*\text{OH}$ remains favorable ($\Delta G = -0.68$ eV). The conversion of $^*\text{NOCO}^*\text{OH}$ to $^*\text{NOCO}$ via hydrogenation-dehydration is identified as the potential-determining step (PDS) for urea synthesis on $\text{Fe-W}_{18}\text{O}_{49}$ with a highest ΔG value of 0.46 eV. This intermediate has been experimentally detected by synchrotron radiation Fourier-transform infrared spectroscopy in related systems.^[40] Further protonation and dehydration steps lead successively to $^*\text{NHOHCO}$, $^*\text{NHCO}$ and $^*\text{NH}_2\text{CO}$, with the protonation of $^*\text{NHCO}$ to $^*\text{NH}_2\text{CO}$ being slightly endergonic with a ΔG of 0.19 eV. The second C–N coupling, $^*\text{NH}_2\text{CO} + \text{NO} \rightarrow$

$^*\text{NH}_2\text{CONO}$, is highly exothermic, followed by further hydrogenation to release urea. Comparison of the PDS barriers across the TM-doped systems reveals that $\text{Fe-W}_{18}\text{O}_{49}$ exhibits the lowest energy requirement (0.46 eV), followed by Zn (0.59 eV), Co (0.60 eV), Cu (0.75 eV), and Ni (1.67 eV). This trend indicates $\text{Fe-W}_{18}\text{O}_{49}$ as the most active catalyst among the series.

To further validate the feasibility of $^*\text{NO} + \text{CO}_2 \rightarrow ^*\text{NOCO}_2$, the charge density difference of $^*\text{NOCO}_2$ intermediates on three promising TM- $\text{W}_{18}\text{O}_{49}$ systems (TM = Fe, Co, Zn) are explored (See Figure 7). The plots show pronounced electron depletion around the C atom (cyan regions) and electron accumulation around the N atom (yellow

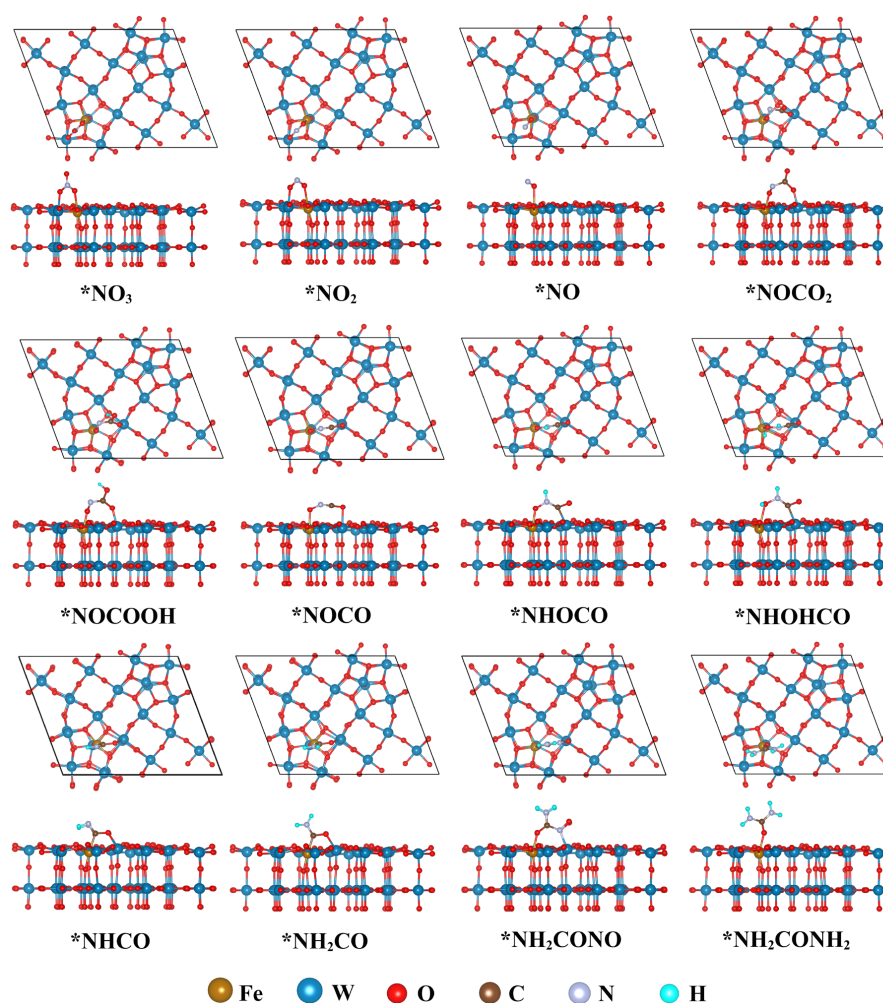
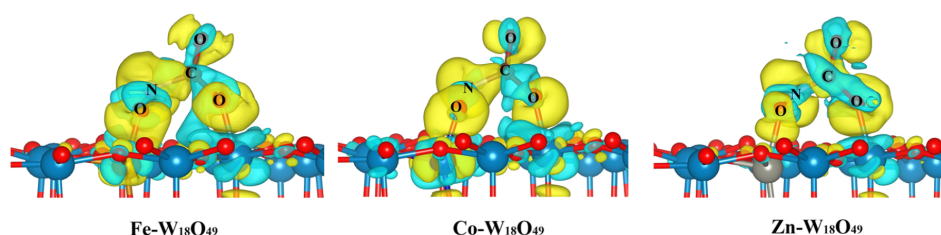


Figure 6 Optimized reaction intermediates for catalytic urea synthesis on $\text{Fe-W}_{18}\text{O}_{49}$



Iso-surface value is $2 \text{ e}^- \text{ nm}^{-3}$

Figure 7 Charge density difference of the key $^*\text{NOCO}_2$ intermediates on TM- $\text{W}_{18}\text{O}_{49}$ (TM = Fe, Co, Zn) surfaces

regions), with significant electron density localized along the newly formed C—N bond (yellow regions). This charge redistribution confirms substantial electron transfer between CO_2 and $^*\text{NO}$, supporting the feasibility of direct C—N coupling *via* $^*\text{NOCO}_2$ formation.

The Gibbs free energy diagram and the optimized structures of the reaction intermediates for the electrocatalytic synthesis of urea on the pristine $\text{W}_{18}\text{O}_{49}$ system are also computed (See Figures 8 and 9) for comparison. While NO_3^- adsorption is even stronger ($E_{\text{ads}} = -4.10$ eV), the subsequent catalytic pathway is less efficient, with the PDS ($^*\text{NHOCO} \rightarrow ^*\text{NHOHCO}$) exhibiting a higher barrier of

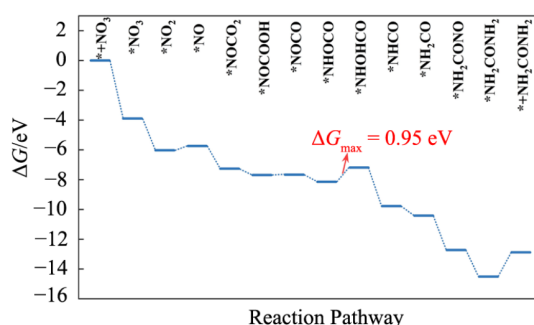


Figure 8 Gibbs free energy diagram for urea production on $\text{W}_{18}\text{O}_{49}$

0.95 eV. In contrast, TM doping not only moderates NO_3^- adsorption but also shifts the PDS to the $^*\text{NOCO}_2\text{H} \rightarrow ^*\text{NOCO}$ step, with significantly reduced barriers (0.46 eV for Fe, 0.60 eV for Co, 0.59 eV for Zn). This marked lowering of the rate-limiting barrier highlights the essential role of the heterometallic doping in enhancing the catalytic activity for urea synthesis.

3.4 Electrocatalytic selectivity of TM- $\text{W}_{18}\text{O}_{49}$ for urea production

In addition to activity, catalytic selectivity is a critical criterion for evaluating the performance of electrocatalysts. For the three most promising TM- $\text{W}_{18}\text{O}_{49}$ systems (TM = Fe, Co, Zn), we systematically assessed their selectivity toward urea synthesis by examining two major competing pathways: nitrate reduction to ammonia (NO_3RR) and the hydrogen evolution reaction (HER).^[44-47]

The reaction pathways for NO_3^- reduction to NH_3 were investigated on Fe-, Co- and Zn- $\text{W}_{18}\text{O}_{49}$ surfaces as shown in Figures 10a–10c, and the optimized structures on Fe- $\text{W}_{18}\text{O}_{49}$ surface are shown in Figure 11. The PDS in all three systems is identified as the hydrogenation of $^*\text{NO}$ to $^*\text{NOH}$, with the maximum ΔG values of 0.32 eV (Fe), 0.38 eV (Co)

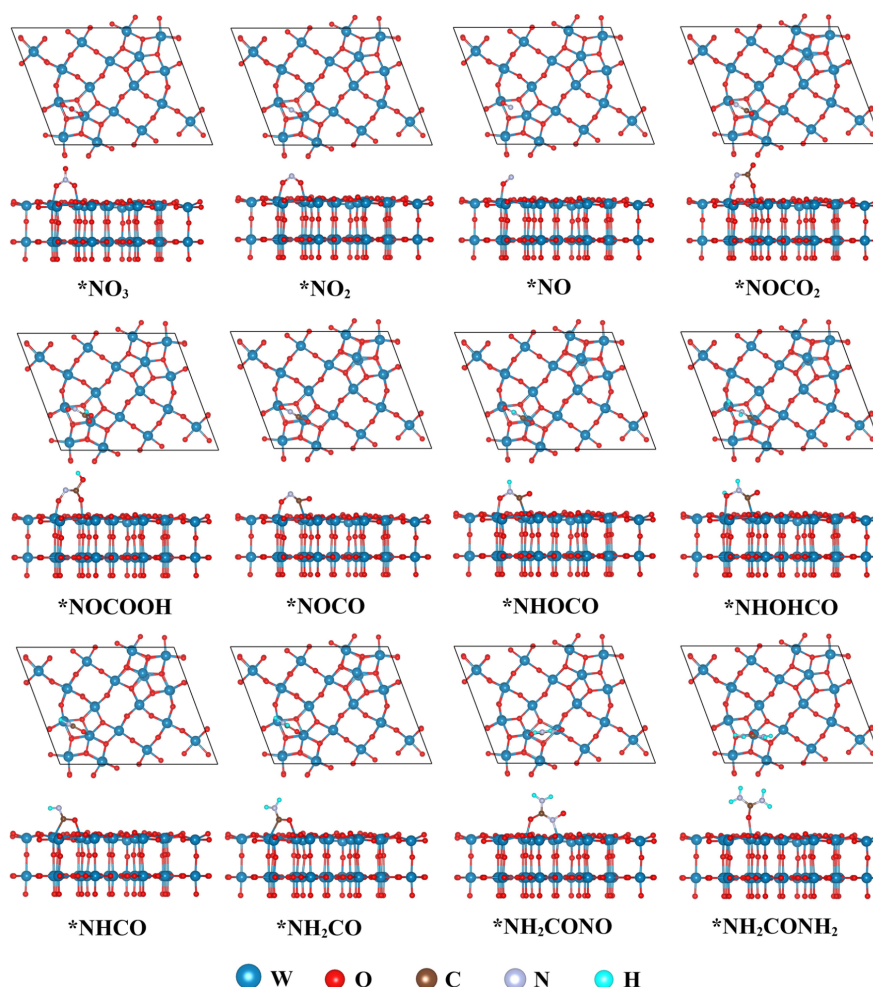


Figure 9 Optimized reaction intermediates for urea production on $\text{W}_{18}\text{O}_{49}$

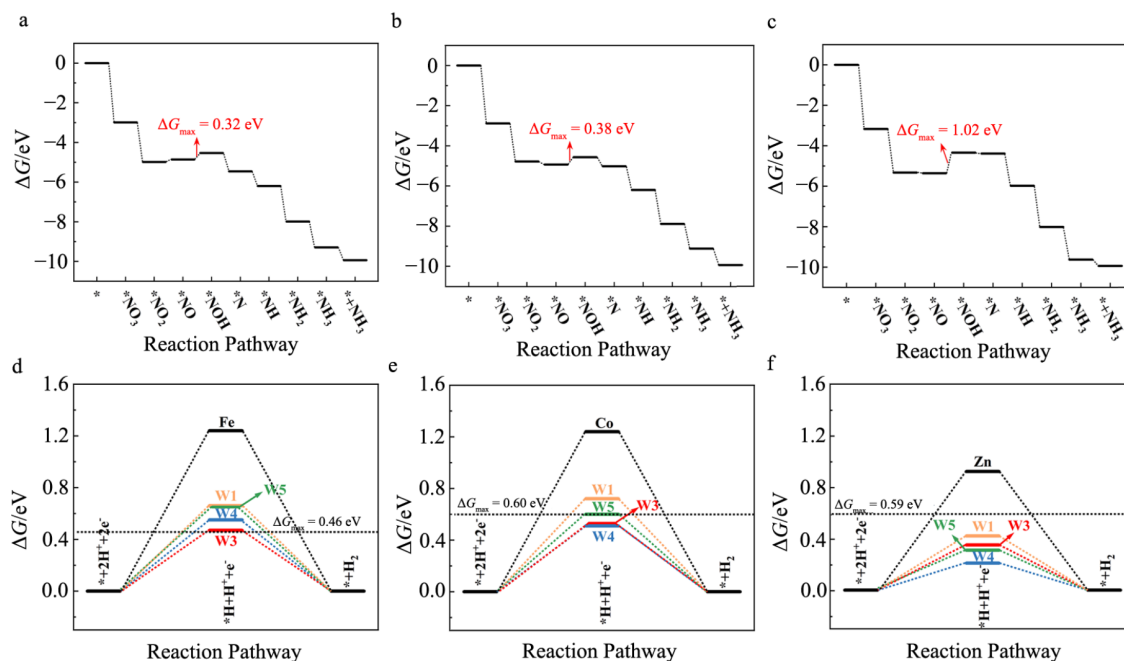


Figure 10 Gibbs free energy diagrams for the reduction of NO_3^- to NH_3 (a–c) and Gibbs free energy diagrams for the HER on $\text{TM-W}_{18}\text{O}_{49}$ (TM = Fe, Co, Zn) surfaces (d–f)

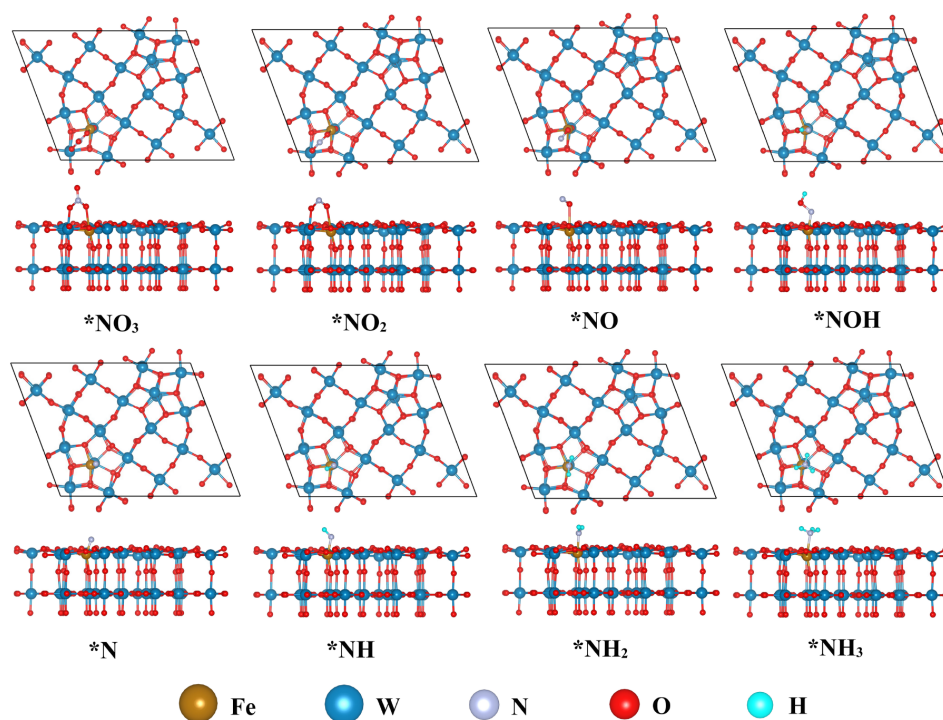


Figure 11 Optimized reaction intermediates during the formation of NH_3 on the $\text{Fe-W}_{18}\text{O}_{49}$ catalyst

and 1.02 eV (Zn). In contrast, the first C–N coupling step ($\text{*NO} + \text{CO}_2 \rightarrow \text{*NOCO}_2$) exhibits significantly lower or negative ΔG values: -0.46 eV for Fe, -0.16 eV for Co and 0.22 eV for Zn. These results clearly indicate that the coupling between *NO and CO_2 is thermodynamically more favorable than the over-reduction of *No to *NOH , thereby effectively suppressing the undesired NH_3 pathway. Furthermore, the second C–N coupling step ($\text{*NH}_2\text{CO} + \text{NO} \rightarrow$

$\text{*NH}_2\text{CONO}$) is highly exothermic, with ΔG values of -3.25 , -2.11 , and -1.88 eV for Fe, Co, and Zn, respectively, reinforcing the thermodynamic drive toward urea formation rather than NH_3 release.

The HER activity was evaluated at various surface sites, including the doped TM atoms and surrounding W sites (See Figures 10d–10f). The calculated hydrogen adsorption energies $E_{\text{ads}}(\text{H})$ are positive across all examined sites, in-

dicating unfavorable *H adsorption and weak HER activity. For instance, in the Fe-W₁₈O₄₉ system, $E_{\text{ads}}(*\text{H})$ values are 1.04 eV at the Fe site, and range from 0.27 to 0.48 eV at adjacent W sites. In comparison, NO₃[−] adsorption energies are strongly negative (E_{ads} for NO₃[−] < −3.0 eV), suggesting that NO₃[−] preferentially occupies the active sites over *H. This site-blocking effect further inhibits HER and enhances selectivity toward nitrate reduction and subsequent C–N coupling.

Collectively, the energetic comparisons demonstrate that TM-W₁₈O₄₉ systems, especially Fe-W₁₈O₄₉, exhibit high intrinsic selectivity for urea synthesis. These findings underscore that heteronuclear TM-W dual-site engineering not only enhance activity but also effectively tunes selectivity, positioning Fe-W₁₈O₄₉ as a promising candidate for efficient and selective electrocatalytic urea production from NO₃[−] and CO₂.

4. Conclusions

This study systematically evaluated a series of heteronuclear transition-metal-doped W₁₈O₄₉(010) surfaces for electrocatalytic urea synthesis from NO₃[−] and CO₂ using first principles calculations. The incorporation of transition metals into the W₁₈O₄₉ lattice induces significant charge transfer and electronic modulation, which collectively enhance both structural stability and catalytic functionality. It is found that heteronuclear TM-W diatomic sites serve as highly effective active centers, exhibiting stronger NO₃[−] adsorption and activation. Mechanistic analysis reveals that urea formation proceeds through two key C–N coupling steps: *NO + CO₂ → *NOCO₂ and *NH₂CO + NO → *NH₂CONO. Among all systems studied, Fe-doped W₁₈O₄₉ exhibits the highest catalytic activity with a remarkably low limiting potential of −0.46 V, along with outstanding selectivity by effectively suppressing competing NH₃ formation and hydrogen evolution. This work elucidates the essential role of heteronuclear dual-metal synergy in enhancing both activity and selectivity toward urea electrosynthesis. The insights provided not only deepen the mechanistic understanding of C–N coupling on bimetallic oxide surfaces but also establish a theoretical basis for rational design of high-performance catalysts.

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电催化尿素合成中的双金属协同效应：Fe掺杂W₁₈O₄₉(010)催化CO₂与NO₃⁻耦合的机理研究

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摘要 电催化二氧化碳(CO₂)与硝酸盐(NO₃⁻)共还原制备尿素是一种兼具环境与能源双重效益的策略, 既能替代高能耗的Bosch-Meiser工艺, 又可同步实现污染物转化。本文基于第一性原理计算, 系统研究了一系列过渡金属掺杂W₁₈O₄₉(010)表面(TM-W₁₈O₄₉, TM = Fe, Co, Ni, Cu, Zn)对尿素合成的催化性能。结果表明, Fe掺杂W₁₈O₄₉具有最优的电催化活性, 其限制电压仅为-0.46 V, 远低于未掺杂体系的-0.95 V, 且表现出优异的选择性, 能有效抑制硝酸盐还原为氨和析氢竞争反应。机理研究表明, 掺杂过渡金属与邻近W位点构成异核双金属协同活性中心, 共同促进NO₃⁻吸附活化, 进而驱动关键C—N耦合步骤。本研究不仅揭示了Fe-W₁₈O₄₉体系的反应路径与活性位点协同机制, 也为设计高效双金属氧化物尿素电催化剂提供了理论依据。

关键词 尿素电合成; 双金属协同; 异核掺杂; C—N耦合