Cooperative single-atom active centers for attenuating linear scaling effect in nitrogen reduction reaction

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ABSTRACT: Cooperative effects of adjacent active centers are critical for single-atom catalysts (SACs) as active site density matters. Yet how it affects scaling relationships in many important reactions like nitrogen reduction reaction (NRR) is underexplored. Herein we elucidate how the cooperation of two active centers can attenuate the linear scaling effect in NRR, through the first-principle study on 39 SACs comprised of two adjacent (~4 Å apart) four N-coordinated metal centers (MN$_2$ duo) embedded in graphene. Bridge-on adsorption of dinitrogen-containing species appreciably tilts the balance of adsorption of N$_2$H and NH$_2$ towards N$_2$H and thus substantially loosens the restraint of scaling relations in NRR, achieving low onset potential (V) and direct N=N cleavage (Mo, Re) at room temperature, respectively. The potential of MN$_2$ duo in NRR casts new insight into circumventing limitations of scaling relations in heterogeneous catalysis.

Heterogeneous catalysis lies at the heart of the chemical industry. The ideal scenario for heterogeneous catalysis, as illustrated by the Sabatier principle, seeks a delicate balance between the activation of reactants and the desorption of products. Yet for most reactions involving multiple intermediates, scaling relationships between adsorption strengths of different intermediates make such a balance difficult to achieve, limiting optimization of catalysts. Breaking scaling relations is crucial for heterogeneous catalyst design. Nørskov and co-workers have suggested using multiple active centers to achieve it based on the first-principle calculations, which is supported by two recent experimental studies. However, the ambiguity, and complexity of structures of active centers in heterogeneous catalysis make it difficult to gain a straightforward and precise understanding on how catalysts could work around the restraint of scaling relations posed to reactions. A simpler catalyst model with a well-defined structure of the active center would be helpful to decipher it.

The emerging single-atom catalysts (SACs) combining the merits of both homogeneous and heterogeneous catalysts have demonstrated excellent performances in a number of different reactions. Because SACs possess simple and unified active centers with well-defined composition and coordination environments, they are deemed an ideal type of catalysts model to provide mechanistic insight into heterogeneous catalysis. Particularly, the advent of high-density SACs due to the rapid advance of synthetic technologies and precise control of inter-site distance would facilitate the study of cooperative effects of multiple active centers. The synergetic effects between adjacent active sites on heterogeneous catalysis have drawn increasing attention in experimental work. In parallel, the computational approach plays an indispensable role in dissecting mechanisms and structure-property relationships associated with SACs. Previously, we have conducted a first-principle study on cooperative communications between two neighboring active centers, and impacts of active site density on oxygen reduction reaction (ORR) and nitrogen reduction reaction (NRR) respectively, which has prompted ourself to continue the exploration of cooperative single-atom active centers.

In the present work, we employed high-density SACs as model systems to systematically investigate impacts of multiple active centers on scaling relationships between adsorption strengths of different reaction intermediates in electrocatalytic nitrogen reduction reaction (eNRR). eNRR has been inspired by enzymatic catalysis of nitrogenase at mild conditions and regarded as a promising solution of energy-saving nitrogen
fixation.\textsuperscript{31} Unfortunately, it is hampered by the challenge of realizing optimal activation energy ($E_a$) of N\textsubscript{2} and adsorption energy ($\Delta E_{\text{ads}}$) of nitrogen-containing intermediate species simultaneously due to the scaling relations that couple favorable (unfavorable) $E_a$ and unfavorable (favorable) $\Delta E_{\text{ads}}$ together. For eNRR, based on the Bell-Evans-Polanyi principle, the strong coupling between adsorption strength of $^*\text{NH}_2$ and $^*\text{N}_2\text{H}$ ($^*$ denotes adsorbed species) is in the center of scaling relations that undermine catalytic activities.\textsuperscript{8} To surpass this limitation, it requires a decoupling mechanism to allow them to be optimized independently.

**Scheme 1.** Various adsorption configurations of N\textsubscript{2} on (a) MN\textsubscript{4}/G and (b) MN\textsubscript{4} duo/G.

Well-established eNRR mechanisms, however, resolve around associative pathways (Figure S1)\textsuperscript{32} assuming single active center, which adsorbs dinitrogen via either end-on or side-on manners (Scheme 1). Meanwhile, alternative adsorption mode of N\textsubscript{2} via ensemble active centers\textsuperscript{33} has largely been underexplored. Previously, we found an alternative reaction path based on cooperative bridge-on adsorption of N\textsubscript{2} (Scheme 1) by two closely arranged (~6 Å) Mo-N-C sites.\textsuperscript{29} This discovery naturally raised the question that whether the bridge-on manner might initiate a game-changing strategy of NRR.\textsuperscript{29} It then motivated us to explore in this work how the scaling relations evolve from single active center to two cooperative active centers as the bridge-on adsorption pattern of N\textsubscript{2} and other nitrogen species are adopted.

**Figure 1.** Top view of MN\textsubscript{4}/G and MN\textsubscript{4} duo/G models used in this work, with the annotation of the philosophy of building them.

A single metal center coordinated with four nitrogen atoms (shorted as MN\textsubscript{4}) constitutes the essential moiety of many excellent molecular catalysts derived from metal porphyrins and metal phthalocyanines.\textsuperscript{35-37} The marriage of MN\textsubscript{4} active center and two-dimensional carbon support (shorted as MN\textsubscript{4}/C) benefits from the ease of synthesis\textsuperscript{13-16}, which has generated quite a few promising SACs, including NRR catalysts\textsuperscript{38-43}. As shown in Figure 1, we placed two adjacent MN\textsubscript{4} within graphene (shorted as MN\textsubscript{4} duo/G) as a prototype model of high-density MN\textsubscript{4} SACs to investigate how the cooperation of single-atom centers will impact scaling relations in NRR. Note that our MN\textsubscript{4} duo model is different from other dual-atom M-N-C models\textsuperscript{44-48} (Figure S2) in two aspects: (1) our model consists of two well-separated MN\textsubscript{4} centers while others either have a metal-metal bond (essentially dimer) or share coordinating atoms; (2) our model focuses on cooperation between two individual active centers while others emphasize one active center with two interconnecting metal atoms.

The results and discussion are organized into two parts. In the first part, we surveyed the scaling relationship between adsorption strength of $^*\text{NH}_2$ and $^*\text{N}_2\text{H}$ in NRR occurring on 39 different MN\textsubscript{4}/G and MN\textsubscript{4} duo/G (Figure S3), represented by their respective Gibbs adsorption free energies ($\Delta G^*\text{NH}_2$ and $\Delta G^*\text{N}_2\text{H}$), and showed how it appreciably shifts as the adsorption mode of $^*\text{N}_2$ and $^*\text{N}_2\text{H}$ varies from end-on to side-on to bridge-on. Equivalently, the significant changes of scaling relations for bridge-on mode were demonstrated in the form of a favorable shift of the volcano plot. In the second part, under the guidance of altered scaling relations, we investigated several potential NRR catalysts, and achieved low onset potential (V) and direct N-N cleavage (Mo, Re) at room temperature (energy barrier < 0.85 eV), respectively. Our results demonstrate the importance of cooperation of monodispersed active centers, which casts new insight into the rational design of SACs for NRR at mild conditions.

**RESULTS AND DISCUSSION**

After building two different sets of MN\textsubscript{4} type SACs: MN\textsubscript{4}/G and MN\textsubscript{4} duo/G (M=transition metals and main group IIIA-VA metals), we first examined their stabilities in terms of thermodynamic stability represented by formation energy ($E_f$) and electrochemical stability represented by dissolution potential ($U_{\text{diss}}$). The majority of them are found to be thermodynamically stable (See Figure S4, Table S1, and associated text in Supporting Information). Since we used the atomic energy in bulk metal as the reference state of the metal, the assignment of “unstable” in the sense of formation energy does not mean it would decompose or undergo aggregation. We expected a large energy barrier for metal migration from one site to another will prevent them from clustering.\textsuperscript{29} Further, as we explore the scaling relationship of adsorption of different intermediates of NRR, these seemly “unstable” MN\textsubscript{4} duo models are all valuable data points that can help sketch the whole picture we need.

All possible adsorption patterns of N\textsubscript{2} as illustrated in Scheme 1 were investigated for all MN\textsubscript{4} and MN\textsubscript{4} duo models. The main group metals of interest could not effectively activate
adsorbed N₂, because they invoke physisorption or very weak chemisorption. Transition metals develop five different scenarios for the adsorption of N₂ (Table S2). In the rest of presentation, only MN₄ and MN₅ duo enabling substantial chemisorption of N₂ will be examined in the study of scaling relations of NRR intermediates.

For associative NRR pathways, the first (*N₂ + H⁺ + e⁻ → *N₂H) and sixth (*NH₂ + H⁺ + e⁻ → *NH₃) reductive hydrogenation steps are the most likely potential-limiting steps. Their respective free energy changes (ΔG₁ and ΔG₆) are coupled through an inversely proportional relationship. Since ΔG₁ and ΔG₆ scale well with ΔG*N₂H for better ΔG*NH₂, respectively (Figure S5), the key scaling relations in NRR eventually fall onto ΔG*N₂H and ΔG*NH₂.

Figure 2. (a) The scaling relationship between ΔG*N₂H and ΔG*NH₂ for end-on adsorption mode on MN₄/G. (b) The differential charge density profiles of end-on *N₂H and *NH₂ by VN₄/G and YN₄/G with an isosurface value of 5×10⁻³ e Å⁻³. Yellow and blue bubbles represent charge accumulation and depletion, respectively. (c) Projected crystal orbital Hamilton population (pCOHP) between the metal centers (V and Y) and the nitrogen adatom. The values of integrated COHP (ICOHP) are shown in red bold italics.

On MN₄/G, as expected, the adsorption of NH₂ scales well with N₂H in end-on mode (Figure 2a), in line with their scaling relationship established on pure metals surfaces. The transition metals can be divided into two groups based on two respective fitting lines. Group 1 (labels in blue) includes the elements in groups IB-IVB, while group 2 (labels in red) contains those in groups VB-VIIIB. (Figure S6) Note that the balance between adsorption of N₂H and NH₂ shifts towards N₂H from group 1 to group 2, which can be interpreted by the amount of charge transfer from metal to nitrogen species (Figure 2b) based on Bader charge profile and the bonding strength between them (Figure 2c) using the integrated crystal orbital Hamilton population (ICOHP) values (more negative value indicates stronger bonding). Take V and Y for example, more negative charges transfer from V to N₂H than to NH₂, while less from Y to N₂H than NH₂; the M-N bonding interaction is appreciably stronger in MN₄-N₂H than in MN₄-NH₂ for V, while it’s weaker in the former than the latter for Y. The same distinction between group 1 and 2 can be found on all types of adsorption mode on both MN₄/G and MN₅ duo/G (Figure S7). Since preferable enhancing the adsorption of N₂H over NH₂ is favorable to mitigate the uphill energetics of activating the adsorbed N₂ and producing NH₁ from NH₂, we then focus on the study of transition metals in group 2 in the rest of work.

From MN₄/G to MN₅ duo/G, the scaling relationships between ΔG*N₂H and ΔG*NH₂ in end-on and side-on adsorption modes do not change significantly (Figure 3), as only one metal center bonds with adsorbates. However, bridge-on adsorption of N₂H on MN₅ duo/G appreciably alters the landscape of scaling relations (Figure 3a). As Figure 3a shows, bridge-on mode appreciably reduces the slope and shifts up the intercept of scaling line relative to end-on mode while side-on mode reduces slope at the cost of shifting down the intercept. Note that smaller slope and higher intercept values enable strengthening adsorption of N₂H much more than NH₂, which facilitates dinitrogen activation without impeding the final reductive hydrogenation producing ammonia. Again, the strengthening of N₂H in bridge-on mode relative to end-on and side-on is demonstrated using Bader charge and ICOHP profiles (Figure 3b). Compared to end-on and side-on modes where only one metal center bond with N₂H, bridge-on mode has two collaborative metal centers binding to N₂H, which increases electrons transferred to anti-bonding orbitals of N₂H and overall metal-nitrogen bonding strength.

In addition, ΔG₁ barely scales with ΔG*N₂H (Figure 3c) for bridge-on mode, which is in sharp contrast to the well scaling between the two in end-on and side-on modes. Here the internal energy part plays a dominant role while the entropy factor has negligible contribution (Table S3). The change of dependence of ΔG₁ on ΔG*N₂H can be explained by the change of binding strength from *N₂ to *N₂H. The integral of partial density of states (pDOS) of nitrogen atoms from -3 eV to 0 eV (Fermi level is reset to 0) is an indicator of effective number of electrons involved in the bonding interaction between nitrogen and metal atoms. Thus, the difference of this integral between *N₂ and *N₂H roughly reflects the difference of their binding strength to metal centers. Clearly, bridge-on mode has the smallest difference while end-on and side-on bear comparable changes (Figure 3d). As two cooperative metal centers accommodate dinitrogen-containing species together, they not only bind them stronger but also mitigate the uphill energetics of first dinitrogen hydrogenation. Consequently, in bridge-on associated NRR pathways, ΔG₁ and ΔG₆ are decoupled (Figure S8), creating room for substantial improvement of overall catalytic activity, as seen in the volcano plots of NRR occurring on MN₅ duo (Figure 4).

Based on the volcano plot associated with bridge-on adsorption mode (Figure 4c), we have identified four selected MN₅ duo/G models (M = Mo, Re, V, Os) as potential NRR catalysts. Although Tc appears to be the closest element to the
vertex of volcano curve, it has to be excluded because it is radioactive. Then, for OsN$_4$ duo/G, initial N$_2$ adsorption adopts an end-on rather than bridge-on mode (Table S4). Thus, we skipped Os as well. In the rest of presentation, we mainly discussed Mo, Re, and V. Intriguingly, V, Mo, and Re are in one diagonal line in the periodic table, which may account for their similar catalytic activities in NRR. In addition to homonuclear MN$_4$ duo/G models, we have also considered heteronuclear MN$_4$ duo/G models in the form of hybrid MN$_4$. Therefore, we have a total of six MN$_4$ duo/G models, including VN$_4$ duo, MoN$_4$ duo, ReN$_4$ duo, VN$_4$-MoN$_4$, MoN$_4$-ReV$_4$, and ReV$_4$-VN$_4$.

Figure 3. (a) The scaling relationships between $\Delta G^{N_2H}$ and $\Delta G^{N_2H}$ as N$_2$H is adsorbed on MN$_4$ duo/G via end-on, side-on, and bridge-on modes, respectively. (b) The differential charge densities of *N$_2$H in bridge-on, side-on, and end-on (from left to right) adsorption modes by VN$_4$ duo/G with an isosurface value of 5x10$^{-3}$ e Å$^{-3}$, and their respective pCOHP between two V atoms and the nitrogen adatoms. Yellow and blue bubbles represent charge accumulation and depletion, respectively. The values of ICOHP are shown in red bold italics. (c) The scaling relationships between $\Delta G^{N_2H}$ and $\Delta G^1$ as both N$_2$ and N$_2$H are adsorbed on VN$_4$ duo/G via, respectively. (d) Electronic densities of states of *N$_2$ (up) and *N$_2$H (down) adsorbed via end-on, side-on, and bridge-on modes on VN$_4$ duo/G, respectively.

Figure 4. The scaling relationships between $\Delta G^1$ and $\Delta G^{N_2H}$ (red line) and between $\Delta G^6$ and $\Delta G^{N_2H}$ (black line) for end-on, side-on, and bridge-on (from left to right) adsorption modes of *N$_2$ and *N$_2$H. The blue dash line in each panel indicates the theoretical lower bound of energetics of presumable potential-limiting steps of NRR in respective adsorption mode.
Using these models, we calculated the full NRR pathways starting from bridge-on adsorption and obtained the onset potential of NRR that signifies the activity of the catalyst of interest. We first examined the adsorption energies of bridge-on adsorbed N$_2$, associated charge redistribution, and geometric changes of reactant-active center complexes. As shown in Table S5, the computed binding energies are between -1.46 and -1.82 eV for bridge-on adsorption, accompanied by substantial charge transfer (0.59 – 0.93 |e| by Bader charge analysis) from both two MN$_4$ sites to N$_2$. The corresponding charge distribution is also demonstrated by the differential charge densities of N$_2$-MN$_4$ duo binding complexes (Figure S9), which illustrates electron gain in the antibonding orbital of N$_2$. As a result, the adsorbed N$_2$ is activated, with an appreciable stretching of N-N bond from 1.11 Å (free N$_2$ in the gas phase) to 1.18 ~ 1.23 Å.

Figure 5. The reaction profile of the bridge-on adsorption initiated NRR pathway on VN$_4$ duo/G model. Roman numbers denote all reaction species along the pathway.

Then we investigated the N≡N bond dissociation following the bridge-on adsorption. The transition state structures are showing in Figure S10. Remarkably, 3 out of 6 selected models, including MoN$_4$ duo, ReN$_4$ duo, and MoN$_4$-ReN$_4$, enable direct N≡N bond breaking with a reaction barrier below 0.91 eV (Table S6), a well-documented threshold for chemical reactions available at room temperature. This unusual phenomenon suggests a dissociative NRR mechanism, in sharp contrast to common N≡N bond dissociation aided by reductive hydrogenation seen in associative NRR pathways. Intriguingly, this pathway will avoid the formation of N$_2$H, one of two key intermediate species in NRR, suggesting the possibility of circumventing the well-established scaling relationship for NRR by direct N≡N bond dissociation through the joint effort of two adjacent active centers.

To understand it, we adopted the N-N distance as the reaction coordinate to understand the trend of energy barriers of N-N dissociation. Intriguingly, the barriers are positively correlated with the distances (Figure S11-a), because a smaller difference of N-N distance between the transition state (TS) and initial state will result in a smaller barrier for N-N bond dissociation. This is typical for an early TS, whose structure is close to the corresponding initial state. Then we examined the relationship between the stabilities of all six models and the corresponding energy barrier of TS and found that the lower stability of the catalyst results in a smaller energy barrier (Figure S11-b). Since the ReN$_4$ duo is the least stable one among these six models, it has the lowest direct N$_2$ dissociation barrier. Similarly, MoN$_4$ duo and MoN$_4$-ReN$_4$ enables direct N$_2$ dissociation at room temperature for their relative lability. The direct N≡N breaking aided by bridge-on adsorption may open a new possibility of breaking scaling relationships applied on NRR, which will be investigated in the future. In contrast, as the stabilities increase, which are the cases of VN$_4$ duo, VN$_4$-MoN$_4$, and VN$_4$-ReN$_4$, the dissociative pathway is unfavorable at room temperature; thus, NRR will proceed via associative mechanisms in which N≡N breaking takes place after one or two steps of reductive hydrogenation. Their bridge-on adsorption initiated NRR pathways is similar to the one occurring on MoN$_3$ duo.
embedded in graphene. The balance between stability and lability of these catalysts may be a key factor for determining the preferred reaction pathways of NRR occurring on them.

The full reaction coordinates of NRR with all six of these models are collected in Figure S12 through Figure S17. Based on the Gibbs free energy data therein, we found that VN₄ duo/G possesses the lowest limiting potential (0.18 V) and thus bears the highest theoretical activity. The reaction coordinates are shown in Figure 5. For the strong adsorption, the ΔG° = −214.2 kcal/mol for bridge-on *N₂ is 0.11 eV and the N−N distance is stretched to 1.31 Å. The second reductive hydrogenation (*NNH + e⁻→ *HNHH) is endothermic (ΔG° = +16.0 kcal/mol), with the N−N distance of 1.37 Å. Intriguingly, this bridge-on *HNHH resembles the bridging “diazene” species found in nitrogenase.⁵⁴ ⁵⁵ Then *HNHH dissociates and produces two *NH, each of which is attached to one V atom. The energy barrier (0.78 eV) for this N≡N bond breaking can be easily overcome at room temperature. Then the two *NH alternately undergo reductive hydrogenation steps, producing two *NH₂. Both reductive hydrogenation of *NH₂ and desorption of NH₃ from *NH₂ are thermodynamically uphill. The electrochemical step can be promoted only by applying an external potential. At U = −0.17 V, ΔG° = −214.2 kcal/mol for NH₃ becomes zero, and the uphill energetics is substantially mitigated (Figure 5). This remarkably low limiting potential benefits from the cooperation of two adjacent VN₄ sites that help breaking the scaling relationship of NRR by properly balancing the adsorption energies of *N₂H and *NH₂. For the endergonic (−0.7 eV) desorption of ammonia, we expect that the solvation of ammonia can mitigate the unfavorable energetics because it will stabilize the desorbed ammonia.⁴ ⁴⁴ ⁵⁶ ⁵⁷ Thus, NH₃ desorption may not be a main obstacle in NRR and, hence, is not considered in detail here.

CONCLUSION

In this work, we have conducted a systematic first-principle study on impacts of bridge-on N₂ adsorption by two adjacent MN₄ sites on scaling relationships within electrocatalytic NRR and found the key to attenuate the scaling relations is to create inhomogeneous adsorption between dinitrogen-containing species and nitrogen-containing species.

We confirmed that the scaling relationship between adsorption of N₂H and NH₃ hold for NRR occurring on single active center, regardless of MN₄ or MN₄ duo. Since the room of improvement of NRR activity associated with one active center is limited, we have to go beyond conventional end-on and side-on adsorption modes. Intriguingly, the side-on fashion benefits from different metal-nitrogen bonding patterns for *N₂H and *NH₂, hinting a path for the evolution of NRR catalysts.⁴ ⁴⁴ ⁵⁸ The bridge-on adsorption mode can be viewed as a two-center version of “side-on”. It further widens the gap of metal-nitrogen bonding strengths between *N₂H and *NH₂, enabling us to decouple the optimization of *N₂ + e⁻ + H⁺ → *N₂H and (*NH₂ + e⁻ + H⁺ → *NH₃). Thus, it shows the potential of making substantial progress towards breaking scaling relations in NRR. Importantly, the bridge-on pattern relies on the proximity of two metal active sites, which could well explain other reported promising NRR catalytic systems invoking bridge-on like activation of N₂ by multiple active centers.⁵⁹ ⁶¹

Based on the survey, we then identified VN₄ duo and ReN₄ duo as promising NRR catalysts through associative mechanisms and dissociative mechanisms, respectively. For VN₄ duo, the remarkably low onset potential (0.18 eV) indicates the level of excellent activity of NRR that can be achieved by high-density SACs. For ReN₄ duo, the most appealing feature is the low energy barrier (0.52 eV) of direct N≡N bond dissociation enabling a dissociative mechanism for NRR at room temperature, which for sure will inspire more mechanistic study on dissociative pathways with multiple concerted active centers. We also expect it motivates more exploration on how the delicate balance between stability and lability of active centers would affect the dynamics of N₂ activation process.

In summary, through a comprehensive understanding of scaling relationships for NRR in MN₄-type single-atom catalysts, we found cooperation of two adjacent single-atom active centers can attenuate scaling relation effect and facilitate nitrogen fixation. Although our computational models are based on ideal reaction conditions, we expect our work casting new light on NRR mechanisms with collective active centers will be helpful for the rational design of high-density SACs and prompting mechanistic study on breaking scaling relationships existing in other reactions (e.g. CO₂ reduction⁶² and oxygen reduction reaction) aided by cooperative multiple active centers. We will also continue the investigation of cooperative single-atom active centers under more realistic reaction conditions in the future work.

COMPUTATIONAL DETAILS

All spin-polarized density functional theory (DFT) calculations were performed using the Perdew-Burke-Ernzerhof (PBE)⁶³ functional in conjunction with plane-wave projected augmented wave (PAW)⁶⁴ method as implemented in Vienna ab initio simulation program (VASP)⁶⁵-⁶⁶. The kinetic cutoff energy for the plane-wave basis set was set to be 480 eV. The Gaussian smearing method was adopted with a width of 0.1 eV to describe partial occupancies of each orbital. The first Brillouin zone was sampled by a Monkhorst–Pack scheme with a 3 × 3 × 1 k-point grid. To avoid the interaction between two periodic units, a vacuum space excesses 15 Å was employed. Structures were fully relaxed until the forces were converged to less than 0.02 eV Å⁻¹. The Grimme’s D3 dispersion correction scheme was used to describe the van der Waals interaction. The solvent effect on scaling relations are not taken into account as a previous study showed that no significant change that can alter the scaling relations has been found as solvent effect was incorporated.⁶⁵ More details regarding adopted computational models, calculation of various energy values and selection of energetic descriptors are given in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information
Computational detail, geometrical structures and stability validation of MN\textsubscript{4} and MN\textsubscript{2} duo models, the adsorption energies of N\textsubscript{2}, differential charge densities, various scaling relationships and Gibbs free energy diagrams for NRR occurring on selected MN\textsubscript{4} duo models.

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**Note**

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