Sabatier principle of metal-support interaction for design of ultrastable metal nanocatalysts

Sulei Hu and Wei-Xue Li*

Hefei National Laboratory for Physical Sciences at the Microscale, School of Chemistry and Materials Science, Key Laboratory of Surface and Interface Chemistry and Energy Catalysis of Anhui Higher Education Institutes, CAS Center for Excellence in Nanoscience, iChEM, University of Science and Technology of China, Hefei, China.

*Corresponding author. Email: wxli70@ustc.edu.cn

The stability of supported nanocatalysts is crucial to meet environmental and energy challenges and necessitates fundamental theory to relieve trial-and-error experimentation and accelerate lab-to-fab translation. Here, we report a Sabatier principle of metal-support interaction for stabilizing metal nanocatalysts against sintering based on the kinetic simulations of 323 metal-support pairs using scaling relations from 1252 energetics data. Too strong of an interaction is shown to trigger Ostwald ripening, whereas too weak of an interaction stimulates particle migration and coalescence. High-throughput screening of supports enables the sintering resistance of nanocatalysts reaching the Tammann temperature on homogeneous supports and far beyond it on heteroenergetic supports. This theory substantiated by the first-principles neural network molecular dynamics simulations and experiments paves the way for design of ultrastable nanocatalysts.

The stability of nanomaterials is a matter of life (time) and death in various nanotechnologies, especially for heterogeneous metal nanocatalysts, to meet energy and environmental requirements (1). The instability among others caused by the thermal and/or chemical induced sintering (2) of smaller metal nanoparticles (NPs) into larger NPs with shrinking atomic utilization severely decreases productivity, delays the lab-to-fab translation of highly active nanocatalysts (3), and requires plant shutdown for catalyst replacement or regeneration with large capital costs (4). The rational design of nanocatalysts with sufficient thermal resistance and operando lifetime, in addition to high activity and selectivity, has significant economic and scientific value even for the general nanoscience field (5).

Sintering of metal NPs proceeds via the formation and diffusion of metal atoms and/or metal–reactant complexes [Ostwald ripening (OR)] (6, 7) and/or via particle migration and coalescence (PMC) on the support (Fig. 1A) (8). To mitigate sintering, physical approaches such as spatial confinement and geometric shielding (9) have been used, which involve the incorporation of NPs into 1D tubular or 3D micro/mesoporous materials (10) and the full/partial encapsulation of less reactive thin films with microchannels upon NPs (11). The cost of these approaches is the blockage of active sites and the impeded transport of reactants. Chemically, alteration of metal-support interaction (MSI) is used to stabilize NPs and control the sintering kinetics (12), which is, however, a complex function of the support composition and surface orientation/defects (13), interface structure, lattice mismatch, mixing/alloy phase formation, charge rearrangement (14), and reaction conditions (15). This fact results in a large gap between the sintering kinetics and the underlying MSI and challenges the screening and/or optimization of supports, thereby necessitating expensive trial-and-error experiments (3). To bridge this gap, it is vital to identify the corresponding MSI descriptor and determine the governing rule for the sintering kinetics and develop a design theory to engineer the metal-support interface for ultrastable nanocatalysts.

Here, we report a Sabatier principle of MSI for the stability of supported metal NPs against sintering based on the linear scaling relationship between the particle adhesion energy and atom binding energy with supports, two MSI descriptors for the corresponding OR and PMC processes. Sintering kinetic simulations of 10 transition metals (TMs) and 91 supports (323 metal-support pairs in total) using 1252 energetics data were conducted, and a universal volcanic dependence of the sintering kinetics on MSI was revealed. It was found that the optimal MSI corresponding to the highest stability on homogeneous supports should be neither too strong nor too weak. Too strong of a MSI triggered rapid OR, whereas too weak of a MSI stimulated facile PMC, both of which severely worsened the stability. For supports with the optimal MSI to NPs, the sintering onset temperature is about half of the melting temperature of the bulk metal for typical NPs (~3 nm), substantiated by the long-reported empirical Tamman temperature. The revealed Sabatier principle enables the high-throughput screening of heteroenergetic supports to break the scaling relationship and boost the sintering resistance of the supported NPs far beyond the Tamman temperature.
The theory substantiated by molecular dynamics (MD) simulation based on the first-principles neural network potential (16) and available experiments (17) paves the way for the design of ultrastable nanocatalysts.

**Scaling relationships**

The size growth rate of NPs via OR is determined by the total activation energy \( E_{\text{act}}(\text{OR}) = E_{\text{bs}} - E_c + E_{\text{adh}} \) describing the formation (\( E_{\text{bs}} - E_c \)) of the ripening monomer (herein metal atom) with respect to the cohesive energy \( E_c \) (negative) of bulk metal and its diffusion on the support (18). Both the binding energy \( E_{\text{bs}} \) (negative) and diffusion barrier \( E_{\text{db}} \) (positive) of the metal atom on the support depend on the MSI. To identify the appropriate MSI descriptor, we retrieved 32 TM atoms and 61 supports (292 metal-support pairs in total) from the literature [see supplementary materials (SM) and data S1 to S6], including various pristine oxide compounds, TMs, and thin films, whose \( E_{\text{bs}} \) and \( E_{\text{db}} \) were calculated using density functional theory (DFT). For most of the considered surfaces, especially corrugated oxides and TM surfaces, \( E_{\text{bs}} \) falls statistically in a green strip exhibiting a linear scaling relation with \( E_{\text{bs}}, \) i.e., \( E_{\text{bs}} = k_{\text{bs}} E_{\text{bs}} (k_{\text{bs}} = -0.18, R^2 = 0.86) \) (Fig. 1B). Note that the flat surfaces falling statistically in the purple stripe have a smaller slope. The results could be rationalized by the fact that the diffusion barrier \( E_{\text{db}} \) of metal atom is proportional to its binding strength \( E_{\text{bs}} \) with a slope determined by among other the surface corrugation (more in the SM). This relationship simplifies the activation energy as

\[
E_{\text{act}}(\text{OR}) = k E_{\text{bs}} - E_c \tag{1}
\]

where \( k = 0.82, \) and \( E_{\text{bs}} \) is used as the MSI descriptor for the OR kinetics below.

The size growth rate of NPs via PMC is determined by the particle diffusion barrier \( E_{\text{act}}(\text{PMC}) = E_{\text{pm}} - S^m E_{\text{adh}} \) consisting of the self-activation energy \( E_{\text{pm}} \) of the metal atom on the metal particle surface and the cost of the particle adhesion energy \( E_{\text{adh}} \) (negative) to the support \( (S^m) \) is the area per atom) (19, 20). \( E_{\text{pm}} \) was found proportional to the corresponding \( E_c \) (fig. S1), \( E_{\text{pm}} = -0.33 E_c \) \( (R^2 = 0.95) \), based on the DFT values over more 200 TM pristine surfaces retrieved from the literature (SM and data S1). Thus, the particle diffusion barrier becomes

\[
E_{\text{act}}(\text{PMC}) = -S^m E_{\text{adh}} - 0.33 E_c \tag{2}
\]

where \( E_{\text{adh}} \) as the MSI descriptor for PMC can be calculated by DFT or extracted from experiment. We retrieved the measured contact angle \( \alpha \) of 188 metal-support pairs including 10 late TMs from the literature (data S2), and calculated the corresponding \( E_{\text{adh}} \) using Young–Dupre’s equation and experimental surface energy of bulk metal. Depending on the metal-support pairs, \( E_{\text{adh}} \) varied at a wide range of value from \(-23 \) to \(-327 \) meV/A², though the calorimetric experiments showed that \( E_{\text{adh}} \) is sensitive to the surface cleanliness (21).

For a given metal-support pair, the corresponding \( E_{\text{bs}} \) and \( E_{\text{adh}} \) are highly correlated. To figure out the correlation, we constructed a series of Ag-supported MgO(100) films (22) with thicknesses from 1 to 8 ML (fig. S2) and calculated its \( E_{\text{bs}} \) and \( E_{\text{adh}} \) toward the Au atom and film using DFT (data S3), respectively. They both decreased with the film thickness and exhibited a linear scaling relationship, \( S^m E_{\text{adh}} \approx E_{\text{bs}}/3 \) \( (R^2 = 0.94) \) (fig. S3A). Moreover, we considered another 42 metal-support pairs retrieved from the literature, and the corresponding \( E_{\text{adh}} \) from experiments and \( E_{\text{bs}} \) from DFT both were available (data S3), from which nearly the same relation as above was found (fig. S3B). To rationalize the results, we note that for a given support adhering strongly to a metal particle would be strongly bound to the metal atom, and the energy gain for the adhesion (per atom) of the particle with a larger coordination is smaller than that of the metal atom to the support. Note that for the bulk metals themselves, there are two relevant quantities as \( E_{\text{bs}} \) and \( E_{\text{adh}} \), namely, the cohesive energy \( E_c \) and surface energy \( \gamma_m \). These two quantities were found to follow a similar scaling relationship, \( 2S^m \gamma_m \approx -1/3E_c \) (fig. S4). Normalizing the previous relationship by the latter one, a dimensionless scaling relationship,

\[
E_{\text{adh}}/2\gamma_m = -E_{\text{bs}}/E_c \tag{3}
\]

was introduced \( (R^2 = 0.89; \) more in the SM) and a diagonal line crossing the origin was depicted in Fig. 1C. For the metal-support pair of interest, when either \( E_{\text{adh}} \) or \( E_{\text{bs}} \) was available, Eq. 3 was applied to estimate the unavailable one (fig. S5). With these paired \( E_{\text{adh}} \) and \( E_{\text{bs}} \) values, \( E_{\text{act}}(\text{OR}) \) and \( E_{\text{act}}(\text{PMC}) \) were calculated for the kinetic simulation below (figs. S6 and S7).

The chemical potential \( \Delta_{\text{NP}} \) of metal atoms in NPs with respect to the bulk metal is crucial for the rate of both OR and PMC. According to the Gibbs–Thomson equation, \( \Delta_{\text{NP}} \) is proportional to \( \gamma_m \) of the metal NPs, whose value differs from the bulk value at small size due to the increased ratio of the lower-coordinated atoms exposed. The change in the surface coordination was estimated by counting various constructed Wulff-shaped NPs of different sizes (fig. S8), based on which a size-dependent \( \gamma_m \) was established (fig. S9). For nanoparticle with a given volume on different supports, different \( E_{\text{adh}} \) leads to different \( \alpha \) and radius \( R \) of curvature, and the corresponding \( \Delta_{\text{NP}} \) becomes support-dependent throughout this work (the details in the SM). Using CeO2-x supported Au NPs as an example, the resulting \( \Delta_{\text{NP}} \) values (blue solid) in Fig. 1D were notably lower than those of unsupported NPs (red solid), consistent with the Campbell’s model (blue dashed) (23).
**Sintering volcano on homogeneous supports**

We now turn to the temperature-programmed OR and PMC kinetic simulations of the above 323 metal-support pairs with the same initial average diameter of typical 3.0 ± 0.3 nm (spherical NPs before contact with the supports of interest). During heating, the onset temperature $T_{on}$ corresponding to a 10% decrease in particle number is defined to estimate the thermal resistance against PMC and OR (methodology details in the SM). The simulated $T_{on}$ for PMC was found to linearly increase with the absolute value of $S^2E_{adh}$ (Fig. 2A and fig. S10). Depending on the TMs, the enhanced MSI strength improves the thermal resistance to PMC by 400 to 700 K due to the increase of $E_{act}(PMC)$ (fig. S7). Consistently, the diffusion coefficient of the supported NPs decreases by 5 to 6 orders of magnitude (fig. S11). In contrast, the simulated $T_{on}$ for OR linearly decreased with the absolute value of $E_{bs}$ as shown in Fig. 2B and fig. S12. This trend was observed because $E_{act}$(OR) decreased with the MSI strength (fig. S6) and the thermal resistance to OR was weaken accordingly.

Because both the OR and PMC contribute to the sintering, the effective $T_{on}$ for the overall sintering is determined by the faster one with the lower $T_{on}$. Considering the counter dependence of the OR and PMC rate on MSI and the constraint of the scaling relationship between $E_{adh}$ and $E_{bs}$ (Eq. 3), a volcanic dependence of the effective $T_{on}$ was immediately seen and plotted in Fig. 2C and fig. S13 with respect to $E_{bs}$ or $S^2E_{adh}$, respectively. At the left side of the volcanic peak where the corresponding MSI was strong, OR had a lower $T_{on}$ and faster rate than PMC, irrespective of the TMs considered. On the right side with weak MSI, PMC had a lower $T_{on}$ and dominated the sintering process. At the volcanic peak with the optimal MSI (neither too strong nor too weak), the rate of OR and PMC became balance, but neither of them was facile. The optimum MSI and corresponding peak temperature showed a great dependence on the metal composition: the stronger the optimal MSI ($\sim -3.73$ eV for Ir vs. $\sim -1.67$ eV for Ag) was, the higher the peak $T_{on}$ (1330 K vs. 540 K) was. To unravel the physics underlined, we used the normalized descriptors of $E_{adh}/2T_m$ or $-E_{bs}/E_c$ to replot Fig. 2C. The optimal MSI after normalization became insensitive to the composition and approximated to a constant value of $-0.53$ (Fig. 2D). The constant optimal MSI could be derived approximately by setting $E_{act}$(OR) = $E_{act}$(PMC) (fig. S14), highlighting the key role of the elementary activation in these two processes to the overall sintering.

The $T_{on}$ value for each TM (Fig. 2D) was further normalized by the melting temperature $T_m$ of the bulk metal counterparts, and then replotted vs. the corresponding $a$ value using the Young–Dupre’s equation in Fig. 2E. All the volcanic curves were found nearly overlapping with a peak $T_{on}$ at 0.47 ± 0.02 $T_m$. This overlap was not unexpected because both $T_m$ and the peak $T_{on}$ depended similarly on $E_c$ of the bulk metals (fig. S15). To see the size effect on the volcanic curves, we increased the initial average diameter of the unsupported NPs from 2 to 22 nm. The optimal MSI was not found to be affected by particle size (fig. S16). However, the peak $T_{on}$ for these 10 TMs increased from 0.44 ± 0.01 $T_m$ to 0.67 ± 0.03 $T_m$ (Fig. 2F). These peak $T_{on}$ values were substantiated by the Tammann temperature ($\sim 0.5 T_m$) of the bulk metal counterparts as the long-reported feature that empirically characterized the sintering temperature of materials. Under reaction conditions, the reactant might stabilize the metal atoms to form metal–reactant complexes on the support (6), leading to a metal-reactant interaction dependent volcanic curve as discussed in the SM.

**Sintering volcano for Au NPs on homogeneous supports**

As proof of principle, the sintering of Au NPs that is sensitive to MSI (24) was investigated. The calculated $T_{on}$ over 82 pristine surfaces were plotted vs. the corresponding $E_{bs}$ in Fig. 3A. Ionic compounds, including oxides, fluorides, and nitrides, attained a relatively weak MSI with Au and were mainly distributed on the right side of the volcanic curve. Carbides with noble metal feature binding modestly to Au were distributed on both sides. However, supports dominated by metallic or covalent bonds, such as metal/boride/semiconductor/oxide films, exhibited a strong MSI with Au and were distributed mainly on the left side. Figure 3A also presented the available experimental data for comparison. Specifically, for MgO, Al$_2$O$_3$ and WO$_3$ located on the right side (fig. S17, A and B), sintering was experimentally observed to proceed via PMC, as predicted by the above kinetic theory. In contrast, for GaAs(211)B and ZrB$_2$ on the left side, sintering was observed to proceed via OR, also in agreement with the theory (fig. S17, C and D). Fe$_3$O$_4$(111) had the optimal MSI to Au and was predicted with a peak temperature of 743 K. Indeed, when annealing at a temperature of 773 K, Scanning Tunneling Microscope (STM) revealed simultaneous Au particle agglomeration and atom migration, suggesting that PMC and OR occurred at a comparable rate and neither of them was facile (25). Consistent trends between theory and experiment were also found for industry-related Pt and Rh nanocatalysts (fig. S18). Moreover, STM experiment also observed a preferential OR process for Pd$_{19}$ clusters on Rh(111) with strong metal-metal bond at the interface (26). The agreement with experiments substantiated the trend behavior and underlying mechanism revealed by the kinetic simulations.

The Sabatier principle was further supported by MD simulations using the first-principles neural network potential (16). Twelve oxide surfaces with different compositions and surface structures were constructed to cover a wide range of MSI to Au. (figs. S19 to S23) One small Au$_{69}$ and six large Au$_{157}$ clusters were supported on the constructed surfaces (10 nm × 10 nm) and MD simulations were performed at 800 K for
two of the 82 supports can be regarded as and .

For Ce-terminated CeO$_2$(100) interacting strongly with Au at the left side ($\alpha = 64^\circ$; Fig. 3B), MD simulations revealed Au atoms detachment from the small Au$_{106}$ cluster and diffusion toward large Au$_{157}$ clusters, and no cluster diffusion was observed during the simulation time (movie S1), indicating a typical OR feature. In contrast, for Zr-terminated ZrO(111) interacting weakly with Au ($\alpha = 176^\circ$; Fig. 3D), the small Au$_{106}$ cluster diffused toward the large Au$_{157}$ cluster (Fig. 3G) and there was no atom detachment found, a typical feature involved in PMC (movie S3). For ZrO(100) near the optimal MSI ($\alpha = 84^\circ$; Fig. 3C), neither atom detachment nor cluster migration was observed within the simulation time (Fig. 3F and movie S2), consistent with the volcanic peak exhibiting a higher stability against sintering.

**Beyond Tamman temperature on heteroenergetic supports**

A further increase in thermal stability beyond the volcanic peak, which is crucial for subnanometer metal clusters and high-temperature catalytic reactions, necessitates breaking of the scaling relationship between $E_{\text{adh}}$ and $E_{\text{msi}}$ (Eq. 3). This feature among others can be achieved by constructing a heteroenergetic support $S@W$, where support $S$ at the nanoscale with strong adhesion (large absolute $E_{\text{adh}}$) pins metal NPs to suppress PMC, and support $W$ with weak binding (small absolute $E_{\text{msi}}$) prevents the formation of metal atoms to inhibit OR. As an example, we constructed a heteroenergetic support of CeO$_{2-x}@[ZrO_2(111)]$ (Fig. 4A), where CeO$_{2-x}(111)$ domains containing 15% oxygen vacancies (24) adhering strongly with Au (fig. S24, A to D) were embedded into the matrix of ZrO$_2$(111) binding weakly with Au (fig. S24, E to H). Small Au$_{106}$ and six Au$_{157}$ clusters were deposited on separated CeO$_{2-x}(111)$ domains with a size comparable to that of the Au clusters. On homogeneous ZrO(100) with optimal MSI as confirmed above (Fig. 3, C and F), MD simulation at 800 K indicated that these small clusters became unstable even at the beginning (fig. S25). However, on CeO$_{2-x}@ZrO_2(111)$, neither cluster migration nor atom detachment from Au$_{106}$ were observed (Fig. 4B and movie S4). Note that a dual-oxide support was proposed to increase the diffusion barrier of metal NPs or atoms across the support surface (27).

The revealed Sabatier principle and scaling relationships can enable the high-throughput screening of the heteroenergetic support $S@W$. For the Au NPs of ~3 nm in Fig. 3A, any two of the 82 supports can be regarded as $S$ and $W$ domains in turn, generating 6724 combinations. For each combination, the lower $T_{\text{on}}$ between that attributed to PMC on the $S$ domains and that attributed to OR on the $W$ domains determines the effective $T_{\text{on}}$ of sintering. These $T_{\text{on}}$ values yield a two-dimensional (2D) sintering map with respect to $E_{\text{adh}}$ for $S$ ($y$-axis) and $E_{\text{msi}}$ for $W$ ($x$-axis) (Fig. 4C). The diagonal line from the bottom left to the top right corresponds to the volcanic curve in Fig. 3A with a peak $T_{\text{on}}$ of 743 K. Strikingly, at the bottom right quarter of the 2D map including 1681 heteroenergetic supports with large $|E_{\text{adh}}|$ for $S$ and small $|E_{\text{msi}}|$ for $W$, all the effective $T_{\text{on}}$ exceeded 743 K and had a maximum even up to 1140 K (~0.85$T_{\text{msi}}$). Among others, CeO$_{2-x}@ZrO_2$ and CeO$_{2-x}@Al_2O_3$ were predicted to appear in this area and the effective $T_{\text{on}}$ were 1050 K and 1100 K, respectively. Since the support $W$ bound weakly with metal atoms is also reluctant to form the metal-reactant complexes, influence of reaction conditions on chemical stability of supported metal NPs via the reactant-promoted Ostwald ripening on the corresponding heteroenergetic $S@W$ could be relieved (more in the SM). Indeed, CeO$_{2-x}@ZrO_2$ as a crucial additive has been applied in commercial automotive exhaust catalysts to improve the overall stability under practical application (28).

Highly durable three-way catalysts in size of even dozens of atoms were realized on CeO$_{2-x}@Al_2O_3$ under severe hydro-thermal aging condition at 1173 K, and the corresponding structure can maintain its stability for 24 hours (17). Considering the new active sites might form at the boundaries between nanocatalyst and support, the heteroenergetic supports provides a platform to simultaneously improve the stability, activity, and selectivity of supported nanocatalysts.

**REFERENCES AND NOTES**

11. H. Tang, Y. Su, B. Zhang, A. F. Lee, M. A. Isaacs, K. Wilson, L. Li, Y. Ren, J. Huang,

ACKNOWLEDGMENTS

The authors thank for the comments from Prof. Dr. Charles T. Campbell. Funding: This work was supported by the National Key R&D Program of China (2018YFA0208603), the National Natural Science Foundation of China (91945302, 21903077), Chinese Academy of Sciences (QYZDJ-SSW-SLH054), K. C. Wong Education (GJTD-2020-15), and the China Postdoctoral Science Foundation. The authors thank Supercomputing Center of University of Science and Technology of China and National Supercomputing Center in Zhengzhou.

Author contributions: Conceptualization: W.X.; Supervision: W.X.; Methodology: S.L.; Investigation: S.L., W.X.; Visualization: S.L.; Writing: W.X., S.L. Competing interests: The authors declare no competing interests. Data and materials availability: All data needed to evaluate the conclusions are present in the paper and the supplementary materials and deposited at Zenodo (29).

SUPPLEMENTARY MATERIALS

science.org/doi/10.1126/science.abi9828

Materials and Methods
Supplementary Text
Figs. S1 to S33
Tables S1 to S4
References (30–53)
Movies S1 to S4
Data S1 to S6

13 April 2021; resubmitted 23 August 2021
Accepted 6 October 2021
Published online 4 November 2021
10.1126/science.abi9828
Fig. 1. Sintering mechanism and scaling relations for the energetics. (A) Schematic of PMC and OR of supported metal NPs. (B) The diffusion barrier $E_{ds}$ and binding energy $E_{bs}$ of metal atoms on corrugated surfaces including oxide compounds (red hollow) and transition metals (TMs) (red solid) in the green strip, on flat surfaces including TM(111) (blue solid), MgO films (blue hollow), and graphene on metal (triangle) in the purple strip (SM and data S1). (C) Metal particle adhesion energy $E_{adh}$ (normalized by two times the surface energy $\gamma_m$ of the bulk metal) vs. metal atom binding energy $E_{bs}$ (normalized by the metal bulk cohesive energy $E_c$) (data S2). (D) Chemical potential $\Delta\mu_{NP}$ of the atoms in unsupported spherical NPs under constant (red dashed) and size-dependent (red solid) $\gamma_m$ values and $\Delta\mu_{NP}$ value for CeO$_{2-x}$ supported Au NPs with a contact angle of 43° (blue solid) and that based on Campbell’s model (23) (blue dashed) as a function of the diameter of the unsupported spherical NPs.
Fig. 2. Volcanic curves of the stability of NPs as a function of metal-support interaction (MSI). (A) Calculated onset temperature $T_{on}$ via PMC vs. the metal particle adhesion energy $S m E_{adh}$ during temperature-programmed kinetics at a heating rate of 1 K/s. On each support, the NPs had the same volume as that of the unsupported spherical NPs with an average diameter of 3.0 ± 0.30 nm. (B) $T_{on}$ via OR vs. the metal atom binding energy $E_{bs}$. (C) Sintering $T_{on}$ corresponding to the lower $T_{on}$ between PMC and OR, vs. $E_{bs}$. (D) Sintering $T_{on}$ versus the normalized MSI descriptors of $E_{adh}/2T_m$ or $-E_{bs}/E_c$. (E) Sintering $T_{on}$ normalized by the melting temperature $T_m$ of the bulk metal vs. the contact angle. (F) Peak $T_{on}$ normalized by $T_m$ vs. the initial average diameter. All the data are listed in the SM. Sensitivity analysis of the scaling relationships used and the impact of their uncertainties on the volcanic curves and trend behavior can be found in the SM.
Fig. 3. Volcanic curves of supported Au NPs and MD simulations. (A) Calculated onset temperature of Au NPs (3 nm) vs. Au atom binding energy onto various supports. The black squares indicate the experimental values with error bars of ± 46 K based on the uncertainty in the size distribution and loading (data S4). (B to G) MD snapshots using the first-principle neural network potential at 800 K at $10^5$ time steps of 1 fs for 1 Au$_{299}$ cluster [(B) to (D)] and 7 Au clusters (1Au$_{69}$ + 6Au$_{157}$) [(E) to (G)] on Ce-terminated CeO$_2$(100) [(B) and (E)], Zr-terminated ZrO(100) [(C) and (F)], and Zr-terminated ZrO(111) [(D) and (G)].
Fig. 4. Screening of heteroenergetic supports beyond the volcanic curves. (A) Heteroenergetic support $S@W$ [CeO$_{2-x}$/ZrO$_2$(111)] containing a small area of domains $S$ (CeO$_{2-x}$) with large absolute $E_{\text{adh}}$ to Au clusters surrounded by a large area of domains $W$ (ZrO$_2$) with small absolute $E_{\text{bs}}$ to Au atoms. (B) Snapshot of the MD simulation after 80 ps (800 K) for 1 Au$_{19}$ + 6 Au$_{55}$ clusters on the CeO$_{2-x}$ domains of CeO$_{2-x}@$ZrO$_2$(111). (C) Onset temperature of sintering of the Au NPs (3 nm) supported on the $S$ domains of the $S@W$ support vs. the $E_{\text{adh}}$ value (y-axis) of the Au NPs onto $S$ domains and the $E_{\text{bs}}$ value (x-axis) of the Au atoms onto $W$ domains.