Supporting Information: Adsorb-Agent: Autonomous Identification of Stable Adsorption Configurations via Large Language Model Agent

Janghoon Ock,[†,‡] Radheesh Sharma Meda,[¶] Tirtha Vinchurkar,[†] Yayati Jadhav,[¶] and Amir Barati Farimani[*,¶]

†*Department of Chemical Engineering, Carnegie Mellon University, 5000 Forbes Ave, Pittsburgh, PA 15213, USA*

‡*Department of Chemical and Biomolecular Engineering, University of Nebraska–Lincoln, Lincoln, NE 68588, USA*

¶*Department of Mechanical Engineering, Carnegie Mellon University, 5000 Forbes Ave, Pittsburgh, PA 15213, USA*

E-mail: barati@cmu.edu

Contents

S1 Auxiliary Prompts

We incorporated two types of auxiliary prompts into the Adsorb-Agent: a reasoning question list for the Solution Planner module and a knowledge prompt for the Critic module. The reasoning question list consists of questions that a human researcher might ask when determining stable adsorption configurations. This list guides the Solution Planner to generate solutions tailored to the task. To ensure the generalizability of the method and to fairly implement the Adsorb-Agent, we intentionally exclude explicit knowledge related to surface chemistry, chemical bonding, or system-specific characteristics. The knowledge prompt, on the other hand, provides terminology clarifications for the Critic module. Its purpose is to ensure that the Critic module can make accurate and contextually appropriate revisions during the solution refinement process.

a

- Are the adsorption sites providing the adsorbate with sufficient metal atoms to bond with?
- Is the coordination number appropriate for the adsorbate, considering its bonding preferences and the type of metal surface?
- Are the bonds between the adsorbate and the surface strong enough to ensure stability?
- Does the adsorbate align in such a way that maximizes overlap with the metal's d-orbitals?
- Is there effective charge transfer between the adsorbate and the surface?
- Does the site provide a favorable electronic environment for adsorption, considering factors like work function and electron density?
- Does the local arrangement of metal atoms enhance or diminish the charge transfer between the adsorbate and the surface?
- Are there any charge redistribution effects that could stabilize or destabilize the adsorbate?
- Are there significant differences in reactivity between the possible adsorption sites (e.g., sites dominated by one metal versus another)?
- Does the adsorbate prefer to bind to a more reactive metal atom or a specific combination of metals on the surface?
- Is the top site or bridge site surrounded by similar or different metal atoms, and how does this affect adsorption strength?
- Are mixed-metal environments (involving different metals) providing a balanced interaction, or is one metal type dominating the adsorption behavior?
- Does the adsorbate align in a way that maximizes favorable interactions with the surface atoms?
- Is the side-on or end-on orientation better suited for the type of bonds the adsorbate can form with the metal surface?
- Is the adsorbate able to form bonds with multiple atoms on the surface, enhancing stability?
- Does the chosen site allow for a symmetric and balanced interaction across multiple metal atoms?
- Is the adsorption energy negative and large enough to suggest that the configuration is thermodynamically stable?
- Are there any nearby sites with similar energy, indicating the presence of multiple stable configurations?
- Are there existing studies or data on similar adsorbates on similar surfaces that support this configuration?
- Does the adsorbate behave similarly on other intermetallic or monometallic surfaces, providing a basis for comparison?

b

- On-top Site: The adsorbate binds directly to a single surface atom.
- Bridge Site: The adsorbate simultaneously binds to two adjacent surface atoms.
- Hollow Site: The adsorbate interacts with three or more surface atoms, typically forming a triangular arrangement.
- End-on Orientation: The adsorbate molecule attaches to the surface through one of its terminal atoms.
- Side-on Orientation: The adsorbate interacts with the surface via multiple atoms along its side.
- Site Matching: The adsorption site should correspond to the number of surface atoms available for binding.
- Orientation Alignment: The binding atoms in the adsorbate should match its orientation on the surface.
- The side-on orientation requires multiple binding atoms.
- The end-on orientation requires just one binding atom.

Figure S1: Auxiliary Prompts: **a.** Reasoning question list, **b.** Knowledge prompt.

S2 LLM Modules

The Adsorb-Agent consists of three modules powered by GPT-4o, with user-defined templates implemented through prompt engineering. Code snippets illustrating these templates are provided in Fig. S2. Notably, the Critic module is further divided into two sub-critics: one focused on reviewing surface-related information and the other on adsorbate-related information.

A significant challenge in effectively utilizing an LLM agent is ensuring determinism in the output of a non-deterministic generative LLM. To address this, we incorporated a parser adapter into each module. This adapter modifies the output prompts and extracts the required target information, enabling precise and consistent control over the outputs for our specific applications.

a

```
def solution_planner(model, parser=AdaptSolutionParser):
    solution_planner_prompt = PromptTemplate(
        input_variables=["system", "reasoning_questions"],
        template=(
            "You are an expert in catalyst and surface chemistry.\n"
            "Your task is to find the most stable adsorption configuration "
            "of an adsorbate on the catalytic surface, "
            "including adsorption site type (ontop, bridge, hollow), "
            "binding atoms in the adsorbate and surface, their numbers, "
            "and the orientation of adsorbate (side-on, end-on, etc). "
            "Given the system: {system}, you must operationalize "
            "the reasoning modules {reasoning_questions} to derive "
            "the most stable configuration for adsorption energy identification.\n"
            "You need to provide the most stable adsorption site & configuration "
            "with the adsorption site type, binding atoms "
            "in the adsorbate and surface, the number of those binding atoms, "
            "and the connection of those binding atoms.\n"
            "NOTE: The adsorption site can be surrounded by atoms of the same element "
            "or a combination of different elements. "
            "Avoid generating binding surface atoms by merely listing all atom types.\n"
            "Instead, determine the binding surface atoms "
            "based on the actual atomic arrangement of the surface.\n"
            "Ensure the derived configuration is very specific "
            "and not semantically repetitive,and provide a rationale.\n"
            "Note: Do not produce invalid content. "
            "Do not repeat the same or semantically similar configuration. "
            "Stick to the given adsorbate and catalyst surface."
             ))
    recon = solution_planner_prompt | model.with_structured_output(parser)
    return recon
```

b

```
def surface_critic(model, parser=AdaptCriticParser):
    site_type_prompt = PromptTemplate(
        input_variables=["system", "adsorption_site_type",\
                         "binding_atoms_on_surface","knowledge_prompt"],
        template=(
            "You are an expert in catalyst and surface chemistry.\n"
            "Observations: {system}\n"
            "Adsorption Site Type: {adsorption_site_type}\n"
            "Binding Atoms on Surface: {binding_atoms_on_surface}\n"
            "Knowledge: {knowledge_prompt}\n"
            "Determine whether the site type matches the number of binding surface atoms.\n"
            "If the site type matches, return 1; otherwise, return 0.\n"
                ))
     adapter = site_type_prompt | model.with_structured_output(parser)
     return adapter

def adsorbate_critic(model, parser=AdaptCriticParser):
    orientation_prompt = PromptTemplate(
        input_variables=["system", "binding_atoms_in_adsorbate",\
                         "orientation_of_adsorbate","knowledge"],
        template=(
            "You are an expert in catalyst and surface chemistry.\n"
            "Observation: {system}\n"
            "Binding Atoms in Adsorbate: {binding_atoms_in_adsorbate}\n"
            "Orientation: {orientation_of_adsorbate}\n"
            "Knowledge: {knowledge_prompt}\n"
            "Determine whether the orientation matches the binding atoms in the adsorbate.\n"
            "If the orientation fully matches, return 1; otherwise, return 0.\n"
                ))
    adapter = orientation_prompt | model.with_structured_output(parser)
    return adapter
```

c

```
def binding_indexer(model, parser=AdaptIndexParser):
    prompt_template = PromptTemplate(
        input_variables=["solution", "atomic_numbers"],
        template=(
                 "You are an expert in catalyst and surface chemistry. "
                 "Based on the given description of the adsorption configuration: \n"
                 "Observations: {solution}\n"
                 "Atomic numbers of atoms in the adsorbate: {atomic_numbers}\n"
                 "Your task is to derive the indices of the binding atoms in the adsorbate. "
                 "Provide the answers for the following questions (only answers, do not include the questions in the output):\n"
                 "1. What are the atom indices of the adsorbate that bind to the site? (Answer: list of indices)\n"
                 "Please stick to the provided answer form and keep it concise.\n"
                 "Note: The indices should be 0-based."
                 )
        )
     adapter = prompt_template | (model).with_structured_output(parser)
     return adapter
```

Figure S2: Code Snippets Illustrating the Implementation of the Adsorb-Agent Modules. **a.** Solution Planner; **b.** Critic; and **c.** Binding Indexer.

S3 Results Across Multiple Runs

Table S1 summarizes the results of individual Adsorb-Agent runs alongside detailed slab metadata. The catalyst bulks are obtained from the Materials Project and are identified by their unique Materials Project ID (mpid). Using the pymatgen package, the selected bulks are sliced along specified Miller indices to generate slab surfaces. The shift parameter determines the position of the cut during slab generation, which defines the surface termination. The top site availability indicates whether adsorption sites are accessible on the topmost layer of the slab.

DFT reference values are taken from the Open Catalyst 2020-Dense (OC20-Dense) dataset.[S1] For systems 1 through 14, no exact matches exist in OC20-Dense. The listed DFT values are for reference only and are not used to evaluate the performance of Adsorb-Agent. In our workflow, Adsorb-Agent reduces the initial configuration space, after which the geometries are optimized using EquiformerV2. Accordingly, performance should be compared against the enumeration baseline, which generates a large number of initial configurations and applies the same geometry optimization procedure.

Any discrepancy between the OC20 DFT reference energies and the EquiformerV2-optimized results can arise when comparing only the single lowest-energy configuration from each approach. To robustly incorporate ML-based structural optimization, the comparison should instead follow the AdsorbML framework. Specifically, after relaxing candidate structures using the ML method, one should perform single-point DFT calculations or short DFT relaxations on the k lowest-energy ML-relaxed configurations.[S1] Using this approach, the AdsorbML framework demonstrated that a lower-energy configuration can be identified with a success rate greater than 85% when $k = 5$.

Table S1: System metadata and adsorption energies for individual Adsorb-Agent runs. The table provides detailed system metadata, including the adsorbate SMILES, catalyst chemical symbol, Miller index, bulk Materials Project ID (mpid), and key structural parameters (e.g., shift and top site availability). The "Run" columns display the results from individual Adsorb-Agent runs.

No.	Adsorbate	Catalyst	Bulk mpid	Shift	Top	Adsorption Energy [eV]					Number of Initial Sets (↓)			
						Run 1	Run 2	Run 3	Algorithm	DFT	Run 1	Run 2	Run 3	Algorithm
1	H	Mo_3Pd (111)	mp-1186014	0.167	True	-0.687	-0.682	-0.925	-0.941 ± 0.002	-	9	4	7	59
2	NNH	Mo_3Pd (111)	mp-1186014	0.167	True	-1.370	-1.041	-1.383	-0.903 ± 0.117	-	14	5	9	51
3	H	Pd_3Cu (111)	mp-1184119	0.063	True	-0.379	-0.384	-0.377	-0.398 ± 0.017	-	18	15	17	98
4	NNH	Pd_3Cu (111)	mp-1184119	0.063	True	0.741	0.753	0.740	0.867 ± 0.072	-	19	20	13	78
5	H	Cu_3Ag (111)	mp-1184011	0.063	True	0.030	-0.069	-0.017	-0.072 ± 0.002	-	22	26	16	98
6	NNH	Cu_3Ag (111)	mp-1184011	0.063	True	1.456	1.583	1.472	1.500 ± 0.002	-	18	13	19	56
7	H	Ru_3Mo (111)	mp-975834	0.167	True	-0.587	-0.587	-0.584	-0.586 ± 0.050	-	15	16	20	94
8	NNH	Ru_3Mo (111)	mp-975834	0.167	True	-0.491	-0.491	-0.487	-0.276 ± 0.003	-	19	18	19	81
9	OH	Pt (111)	mp-126	0.167	True	0.989	0.991	0.991	0.990 ± 0.071	-	7	9	5	54
10	OH	Pt (100)	mp-126	0.250	True	0.993	0.990	0.990	0.991 ± 0.001	-	9	16	6	54
11	OH	Pd (111)	mp-2	0.167	True	0.814	0.813	0.813	0.814 ± 0.001	-	28	15	17	54
12	OH	Au (111)	mp-81	0.167	True	1.407	1.406	1.410	1.409 ± 0.002	-	28	16	26	54
13	OH	Ag (100)	mp-124	0.250	True	0.438	0.441	0.440	0.463 ± 0.009	-	30	21	20	53
14	OH	CoPt (111)	mp-1225998	0.042	True	-0.218	-0.188	-0.220	-0.166 ± 0.046	-	43	41	40	120
15	CH_2CH_2OH	Cu_6Ga_2 (100)	mp-865798	0.248	False	-2.864	-2.989	-1.163	-3.077 ± 0.062	-4.597	42	7	37	66
16	CH_2CH_2OH	Au_2Hf (102)	mp-1018153	0.028	False	-1.924	-3.184	-3.176	-3.761 ± 0.129	-6.113	34	27	23	78
17	$OCHCH_3$	Rh_2Ti_2 (111)	mp-2583	0.083	True	-4.570	-4.562	-4.552	-4.275 ± 0.086	-4.524	23	33	31	62
18	$OCHCH_3$	Al_3Zr (101)	mp-1065309	0.375	False	-4.600	-4.615	-4.634	-4.325 ± 0.052	-3.310	19	22	25	68
19	$OCHCH_3$	Hf_2Zn_6 (110)	mp-866108	0.120	True	-6.066	-5.627	-6.073	-5.443 ± 0.037	-4.048	19	15	20	67
20	$ONN(CH_3)_2$	Bi_2Ti_6 (211)	mp-866201	0.000	True	-3.558	-3.806	-3.000	-2.441 ± 0.103	-4.244	35	36	28	139

S4 System-specific Solutions

Table S2: Solutions for the Complete Set of Systems. One trial from three independent runs is shown as an example.

No.	Adsorbate	Catalyst	Site Type	Surf. Binding Atoms	Ads. Binding Atoms	Ads. Orientation
1	H	Mo_3Pd (111)	hollow	Mo, Mo, Pd	H	end-on
2	NNH	Mo_3Pd (111)	hollow	Mo, Mo, Pd	N, N	side-on
3	H	Pd_3Cu (111)	hollow	Cu, Pd, Pd	H	end-on
4	NNH	Pd_3Cu (111)	hollow	Pd, Pd, Cu	N, N	side-on
5	H	Cu_3Ag (111)	hollow	Cu, Ag, Cu	H	end-on
6	NNH	Cu_3Ag (111)	bridge	Cu, Ag	N, H	end-on
7	H	Ru_3Mo (111)	hollow	Ru, Mo, Mo	H	end-on
8	NNH	Ru_3Mo (111)	bridge	Ru, Mo	N, N	side-on
9	OH	Pt (111)	hollow	Pt, Pt, Pt	O	end-on
10	OH	Pt (100)	hollow	Pt, Pt, Pt	O	end-on
11	OH	Pd (111)	hollow	Pd, Pd, Pd	O, H	end-on
12	OH	Au (111)	ontop	Au	O	end-on
13	OH	Ag (100)	ontop	Ag	O	end-on
14	OH	CoPt (111)	bridge	Co, Pt	O	end-on
15	CH_2CH_2OH	Cu_6Ga_2 (100)	bridge	Cu, Ga	C, O	side-on
16	CH_2CH_2OH	Au_2Hf (102)	bridge	Hf, Au	C, O	end-on
17	$OCHCH_3$	Rh_2Ti_2 (111)	bridge	Ti, Rh	O, C	side-on
18	$OCHCH_3$	Al_3Zr (101)	bridge	Zr, Al	O, C	side-on
19	$OCHCH_3$	Hf_2Zn_6 (110)	bridge	Zn, Hf	O, C	side-on
20	$ONN(CH_3)_2$	Bi_2Ti_6 (211)	bridge	Bi, Ti	N, N	side-on

S5 Comparison of Internal System Prompt Variants

Each module requires an internal system prompt, and there is considerable flexibility in how this prompt is defined. To evaluate the effect of the system prompt, we tested three variations: (1) the base system prompt that specifies the task, (2) a system prompt with an emphasis on geometric considerations, and (3) a system prompt emphasizing electronic characteristics. We then compared the resulting solution prompts across these variations. The exact text is provided in the following text block, where blue highlights the newly added content on top of the base system prompt, and red indicates the responses generated based on the newly added content.

When a new section is added to the system prompt, the agent generates specific content in the full solution prompt. However, the final adsorption configuration summarized at the end of the solution prompt remains consistent across all three prompt variations. Adding specific information to the system prompt may alter the agent's internal chain-of-thought process, but it does not necessarily lead to a different final answer. This observation suggests that the solution prompt is not highly sensitive to changes in the system prompt, which is beneficial for stability. Nevertheless, a more rigorous evaluation of prompt-specific stability should be conducted in future work.

Geometric Emphasis-Aware System Prompt and Full Raw Solution

System prompt:

"You are an expert in catalyst and surface chemistry. Your task is to find the most stable adsorption configuration of an adsorbate on the catalytic surface, including adsorption site type (ontop, bridge, hollow), binding atoms in the adsorbate and surface, their numbers, and the orientation of the adsorbate (side-on, end-on, etc).Given the system: {query}, you must operationalize the reasoning modules {reasoning} to derive the most stable configuration. Provide the final adsorption site type, binding atoms (adsorbate and surface), number of binding atoms, orientation, and a short rationale.

Full raw solution prompt:

To determine the most stable adsorption configuration of the NNH molecule on a Mo3Pd (111) surface, we'll evaluate the system using the specified reasoning modules:

1. **Are the adsorption sites providing the adsorbate with sufficient metal atoms to bond with?**

   The (111) surface is densely packed and typically provides multiple atoms for bonding. This is crucial for adsorbates that can interact with the surface through more than one atom.

2. **Is the coordination number appropriate for the adsorbate, considering its bonding preferences and the type of metal surface?**

   NNH has at least two main interaction sites: the nitrogen atoms. A bridge site on Mo3Pd (111) could allow sufficient coordination with these species.

3. **Is the side-on or end-on orientation better suited for the type of bonds the adsorbate can form?**

   Given NNH, a side-on orientation might allow both nitrogen atoms to interact with the surface, which could stabilize the adsorption through multiple interactions, compared to an end-on orientation that would likely favor only one main interaction point.

4. **Does the chosen site allow for a symmetric and balanced interaction across multiple metal atoms?**

   Hollow sites (FCC or HCP) could facilitate symmetric binding in a side-on configuration, allowing both nitrogen atoms to interact with multiple metal atoms.

5. **Is the adsorption energy negative and large enough to suggest that the configuration is thermodynamically stable?**

   While specific energy calculations are absent, literature suggests that coordinated and symmetric configurations (e.g., side-on over hollow sites) yield stronger binding and more negative adsorption energies.

6. **Are there existing studies or data on similar adsorbates on similar surfaces that support this configuration?**
   Studies of nitrogen-containing small molecules on transition metals indicate that maximizing coordination favors stability. Hollow sites are commonly observed for N_2 and NH_3 adsorption, supporting a similar approach for NNH.

Conclusion:

- **Adsorption site type:** FCC or HCP hollow site on Mo3Pd (111)
- **Binding atoms:** Both nitrogen atoms from NNH with metal atoms (Mo and Pd) at the hollow site
- **Number of binding atoms:** Typically three metal atoms per hollow site
- **Orientation:** Side-on
- **Rationale:** Hollow site allows maximal coordination and symmetric adsorption; side-on orientation facilitates interactions of both nitrogen atoms, aligning with the adsorbate's bonding preferences. Configuration is anticipated to have favorable negative adsorption energy, consistent with similar systems.

Geometric Emphasis-Aware System Prompt and Full Raw Solution

System Prompt:

"You are an expert in catalyst and surface chemistry. Your task is to find the most stable adsorption configuration of an adsorbate on the catalytic surface, including adsorption site type (ontop, bridge, hollow), binding atoms in the adsorbate and surface, their numbers, and the orientation of the adsorbate (side-on, end-on, etc). Given the system:

{query}, you must operationalize the reasoning modules {reasoning} to derive the most stable configuration. Provide the final adsorption site type, binding atoms (adsorbate and surface), number of binding atoms, orientation, and a short rationale. The surface exposes ontop, bridge, and hollow sites of different coordination environments. Analyze which site offers optimal geometric matching between the adsorbate's bonding atoms and the surface atoms. Differentiate possible orientations (side-on, end-on, tilted) by evaluating coordination symmetry and steric compatibility. Identify the most stable configuration accordingly."

Full Raw Solution Prompt:

To determine the most stable adsorption configuration of the NNH molecule on the Mo3Pd (111) surface, we need to consider various factors such as the coordination environment, the bonding preferences of the adsorbate, and established trends in similar systems. Here's a step-by-step analysis using the provided reasoning modules:

1. **Adsorption Sites and Metal Atoms Availability:**
   The Mo3Pd (111) surface exposes different site types: ontop, bridge, and hollow, each offering varying coordination numbers. The hollow site, which typically offers higher coordination, involves three surface atoms and is most likely to provide sufficient metal atoms for bonding with multi-atom adsorbates like NNH.

2. **Coordination Number Appropriateness:**
   NNH adsorption might benefit from a higher coordination environment due to its multi-atom nature. An hcp or fcc type hollow site provides a coordinated environment engaging both Mo and Pd atoms, complementing the bonding needs of N-H.

3. **Orientation Consideration:**

Side-on adsorption is often favorable for molecules that can engage in multi-dentate coordination. Given NNH's structure, positioning it side-on can allow both nitrogen atoms to interact with the surface metal atoms, potentially involving N-N and N-H with different metal atoms for a more stable configuration.

4. **Symmetric and Balanced Interaction:**
   The hollow site enables symmetric interaction across the adsorbate, distributing the bonding stress evenly and potentially engaging both heteronuclear bonds (N–N and N–H) with metal atoms.

5. **Thermodynamic Stability:**
   Although no specific adsorption energy is provided here, for real-world systems, this configuration should ideally result in a negative and significantly large adsorption energy, indicating a strong stable adsorption interaction.

6. **Supporting Evidence from Literature:**
   In literature concerning similar adsorbates on transition metal surfaces, side-on configurations over hollow sites often emerge as stable configurations due to effective multi-bonding interactions.

Final Configuration:

- **Adsorption Site Type:** Hollow site (either hcp or fcc, as both provide maximum coordination)
- **Binding Atoms and Numbers:** Adsorbate: Two nitrogen atoms from NNH; Surface: typically three atoms including Mo and Pd
- **Orientation:** Side-on
- **Rationale:** Hollow site provides sufficient metallic coordination, and side-on orientation allows balanced bonding interactions, consistent with trends for similar

adsorbates.

Electronic (d-Orbitals)-Aware System Prompt and Full Solution

System Prompt:

"You are an expert in catalyst and surface chemistry. Your task is to find the most stable adsorption configuration of an adsorbate on the catalytic surface, including adsorption site type (ontop, bridge, hollow), binding atoms in the adsorbate and surface, their numbers, and the orientation of the adsorbate (side-on, end-on, etc). Given the system: {query}, you must operationalize the reasoning modules {reasoning} to derive the most stable configuration. Provide the final adsorption site type, binding atoms (adsorbate and surface), number of binding atoms, orientation, and a short rationale. Consider how charge transfer and orbital overlap between the adsorbate and surface d-orbitals determine site preference. Evaluate how differences in surface atom electronegativity or composition influence adsorption strength and orientation. Incorporate these electronic interactions when identifying the most stable adsorption geometry and orientation."

Full Raw Solution Prompt:

To determine the most stable adsorption configuration of the *NNH* molecule on the $Mo_3Pd(111)$ surface, we examine the nature of the adsorbate and the surface, focusing on binding sites, coordination, orientation, electronic interactions, and literature precedents.

1. **Adsorption Sites and Coordination:**

   The $Mo_3Pd(111)$ surface has ontop, bridge, and hollow sites (fcc and hcp). *NNH* is linear and prefers multi-metal coordination, favoring bridge or hollow sites.

2. **Coordination and Bonding Preferences:**

   Given the ability of nitrogen to form multi-dentate interactions due to its lone pair of electrons and its preference for higher coordination sites for better stabilization (especially in transition metals), the hollow sites should be considered strongly. The fcc hollow site could provide strong coordination with three metal atoms, optimizing interactions and charge transfer.

3. **Orientation: Side-on vs. End-on:**
   Side-on maximizes interaction and charge transfer for *NNH* at hollow sites, whereas end-on reduces surface contact and is less favorable.

4. **Symmetry and Interaction:**
   Side-on in a hollow site allows symmetric interaction across metal atoms, improving orbital overlap and charge transfer with Mo/Pd d-orbitals.

5. **Thermodynamics (Adsorption Energy):**
   The most stable adsorption should have a significantly negative adsorption energy, reflecting thermodynamic favorability.

6. **Existing Studies and Similar Systems:**
   Literature shows side-on configurations on transition metal alloys are generally stable due to differential charge transfer and enhanced binding.

Final Adsorption Configuration:

- **Adsorption Site Type:** fcc hollow site
- **Binding Atoms:** N atoms from *NNH* and Mo/Pd surface atoms
- **Number of Binding Atoms:** 3 surface metal atoms (2 Mo, 1 Pd)
- **Orientation:** Side-on across the fcc hollow site
- **Rationale:** This configuration allows for maximum orbital overlap and charge transfer between the nitrogen atoms and the surface d-orbitals, optimized by the

mixed Mo/Pd composition which adjusts the electronic environment. The choice of an fcc hollow site provides a high-coordination environment preferred for linear nitrogen adsorbates, supported by typical structures seen in transition metal adsorption studies.

S6 Role of the External Reasoning Prompts

The Adsorb-Agent framework requires an external reasoning prompt about the domain-specific reasoning questions, as illustrated in Fig. 1c. To assess the effect of the external reasoning prompt, we ran the Solution Planner both with and without it. Specifically, we extracted the solution before it was processed by the parser and implemented the Solution Planner without the iterative interaction with the Critic module. This approach allows us to isolate and evaluate the raw outputs of the Solution Planner and directly compare the impact of including or omitting the external reasoning prompt.

Table S3: Comparison of Solution Planner outputs with and without reasoning prompts for Systems 1–4. Note: These results are extracted manually from the raw solution prompt, before parsing and without iteration with the Critic module. They are not the final results used to reduce the configuration search space.

No.	Orientation (Reasoning)	Orientation (No Reasoning)	Site (Reasoning)	Site (No Reasoning)
System 1: H-Mo_3Pd (111)				
1	end-on	unknown	3-fold hollow	hollow
2	end-on	end-on	hollow site (hcp)	hollow (fcc or hcp)
3	unknown	side-on	three-fold hollow	hollow
4	symmetrical	perpendicular	fcc hollow	3-fold hollow
5	end-on	unknown	fcc hollow	hcp hollow site
6	unknown	end-on	fcc hollow site	threefold hollow (fcc hollow site)
7	unknown	end-on	fcc hollow site	hollow site (FCC)
System 2: NNH-Mo_3Pd (111)				
1	side-on	end-on	hollow	bridge
2	end-on	side-on	hollow	hollow site
3	end-on	end-on	bridge	hollow (threefold fcc)
4	side-on	end-on	bridge site	hollow
5	end-on	side-on	hollow	hollow (fcc)
6	side-on	side-on	bridge	hollow
7	end-on Tilted	side-on	fcc hollow site	bridge
System 3: H-$CuPd_3$ (111)				
1	end-on	mixed	fcc hollow, bridge	hollow (fcc)
2	side-on	side-on	fcc hollow site	FCC hollow
3	end-on	on-plane	fcc hollow	fcc hollow site
4	end-on	perpendicular to the triangular plane	3-fold hollow site (fcc type)	hollow
5	mixed	side-on	FCC hollow	fcc hollow
6	end-on	end-on	fcc hollow	fcc hollow site
7	unknown	unknown	hollow	Fcc Hollow Site
System 4: NNH-$CuPd_3$ (111)				
1	end-on	end-on	hollow fcc	ontop
2	side-on	side-on	hollow fcc	hollow
3	side-on	side-on	fcc hollow site	hollow
4	side-on	end-on	hollow	bridge
5	side-on	side-on	fcc hollow site	FCC Hollow
6	side-on	end-on	bridge	hollow
7	side-on	side-on	fcc hollow	hollow (fcc - face-centered cubic)

For System 4, the agent more consistently predicts the adsorbate orientation as side-on when using the reasoning prompt. However, this improvement is not observed across all systems (see Table S3). While the reasoning prompt can aid certain cases, the overall results suggest that similar performance could likely be achieved with a reduced reliance on the external reasoning prompt.

S7 Critic Module Performance

The Critic module evaluates the solution generated by the Solution Planner based solely on the language model's reasoning capability. Although equivalent checks could be implemented using rule-based logic, we intentionally use the language model here to assess its ability to perform adsorption configuration validation end-to-end. For reference, the corresponding rule-based functions for surface sites and adsorbate orientations are shown below:

Algorithm 1 Rule-Based Self-Consistency Check for Surface

Require: site_type (string), n_{surface} (integer)
$s \leftarrow$ lowercase(site_type)
if "hollow" $\in s$ **and** $n_{\text{surface}} \geq 3$ **then**
    return 1
else if "bridge" $\in s$ **and** $n_{\text{surface}} = 2$ **then**
    return 1
else if "ontop" $\in s$ **and** $n_{\text{surface}} = 1$ **then**
    return 1
else
    return 0
end if

Algorithm 2 Rule-Based Consistency Check for Adsorbate

Require: orientation (string), n_{ads} (integer)
$o \leftarrow$ lowercase(orientation)
if "side-on" $\in o$ **and** $n_{\text{ads}} > 1$ **then**
    return 1
else if "end-on" $\in o$ **and** $n_{\text{ads}} = 1$ **then**
    return 1
else
    return 0
end if

We evaluated the accuracy of the Critic module (LLM-based) by comparing its outputs against the ground-truth self-consistency labels obtained from the rule-based checks. Adsorb-Agent was run three times across all twenty systems, and the Critic outputs were assessed for agreement with the rule-based results. For the surface self-consistency evaluation, the Critic correctly matched the rule-based outcome in 98.3% of cases. For the adsorbate self-consistency evaluation, the accuracy was 88.1%. Overall, when considering both evaluations jointly, the Critic module achieved an accuracy of 86.4% (see Table S4).

Table S4: Accuracy of the Critic Module Compared with Rule-Based Self-Consistency Checks

Evaluation Type	**Accuracy (%)**
Surface Self-Consistency	98.3
Adsorbate Self-Consistency	88.1
Overall Consistency	86.4

What is particularly important is that the LLM-based Critic module achieves a high accuracy (98.3%) in assessing surface self-consistency. This matters because the reduction of the initial configuration space is primarily determined by the choice of adsorption sites on the surface. In contrast, the adsorbate binding information is only used during the subsequent placement of the adsorbate. Therefore, occasional inaccuracies in the adsorbate self-consistency evaluation may lead to minor variations in the precise adsorbate placement, but they do not affect the overall reduction of the configuration search space. Moreover, because the adsorbate placement algorithm itself has inherent stochasticity, such slight variations in placement may not meaningfully influence the final configuration outcomes.

References

(S1) Lan, J.; Palizhati, A.; Shuaibi, M.; Wood, B. M.; Wander, B.; Das, A.; Uyttendaele, M.; Zitnick, C. L.; Ulissi, Z. W. AdsorbML: a leap in efficiency for adsorption energy calculations using generalizable machine learning potentials. *npj Computational Materials* **2023**, *9*, 172.