Supplement Materials

Coordination-Layer Engineering of Pt Single Atoms on h-BN for Propane Dehydrogenation via a p-Band Descriptor Validated by Multiscale Modeling and Knowledge-Informed Machine Learning

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Table S1. Summary of Key Calculated Properties for Pt/V_B and Pt/V_N series Catalysts.

Catalyst	Formation Energy, E_f (eV)	Bader Charge on Pt, Pt(e)	Average p-band (eV)	Average ICOHP (eV)
Pt/V_B	0.17	+0.68	-4.626	-3.43
Pt/V_B-C1	0.21	+0.59	-3.791	-3.56
Pt/V_B-C2	0.26	+0.44	-2.775	-3.57
Pt/V_B-C3	0.31	+0.33	-1.986	-3.69
Pt/V_N	0.17	-1.04	-4.151	-3.23
Pt/V_N-C1	0.19	-0.74	-4.317	-3.23
Pt/V_N-C2	0.21	-0.24	-4.773	-3.87
Pt/V_N-C3	0.24	-0.18	-5.435	-3.9

Table S2. Hyperparameter Search Space and Optimal Configuration

Model	Hyperparameter Search Space	B-series Optimal	N-series Optimal
PhysFormer	hidden ∈ {16, 32}, depth ∈ {2, 3}, dropout ∈ {0, 0.2}, lr ∈ {3e-3, 5e-3}, wd ∈ {1e-3, 2e-2}	hidden=32, depth=3, dropout=0.2, lr=5e-3, wd=1e-3	hidden=16, depth=2, dropout=0, lr=3e-3, wd=2e-2
RandomForest	n_estimators ∈ {100, 200, 300}, max_depth ∈ {3, 4, 5, 6}	n_estimators=300, max_depth=4	n_estimators=200, max_depth=5
XGBoost	max_depth ∈ {2, 3, 4}, learning_rate ∈ {0.01, 0.05, 0.1}, n_estimators=500	max_depth=4, lr=0.01	max_depth=2, lr=0.01
Ridge	α = 1.0, with additional inverse temperature feature 1/T	—	—

Table S3. Model Performance Comparison

Series	Model	Train R^2	LOCO R^2
B	PhysFormer	0.98	**0.94**
B	RandomForest	0.99	0.90
B	XGBoost	0.99	0.86
B	Ridge	0.02	-0.01
N	PhysFormer	0.99	**0.96**
N	RandomForest	0.99	0.95
N	XGBoost	0.99	0.93
N	Ridge	0.00	0.00

Table S4. Parameters for RMG input files.

Property	Value
Temperatures	600-1000 K
nSim	7
Pressure	1 bar
Active site	Pt
Surface site density	2.943×10^{-5}, mol/m^2
Specific surface area	1×10^5 m^2 m^{-3}
toleranceMoveToCore, ε_{core}	1×10^{-1}
toleranceKeepInEdge, ε_{core}	0
terminationRateRatio, ε_{rate}	1×10^{-7}
toleranceInterruptSimulation,	1×10^8
maximumSurfaceSites	1
maximumEdgeSpecies	500000
Initial composition	10 % C_3H_8, 10 % H_2, 80 % N_2
Initial coverage	Vacant site fraction = 1.0

Table S5. Calculated first C-H bond activation energy barriers (E_a) for propane and corresponding Turnover Frequencies (TOFs) at 800 K and 1 bar on catalysts with different local coordination environments.

Catalyst Model	Pt Substitution Site	No. of Neighboring C Atoms	E_a (eV)	TOF (s^{-1})
Pt/V_B	B	0	0.31	11.59
Pt/V_B-C1	B	1	0.53	9.49
Pt/V_B-C2	B	2	0.70	6.94
Pt/V_B-C3	B	3	0.96	4.93
Pt/V_N	N	0	0.86	5.57
Pt/V_N-C1	N	1	0.67	7.60
Pt/V_N-C2	N	2	0.61	8.58
Pt/V_N-C3	N	3	0.55	9.53

Table S6. Gibbs free energy for activation of the first C-H bond in each catalyst at 800 K.

Catalyst Model	Gibbs free energy（eV）
Pt/V_B	0.2
Pt/V_B-C1	0.45

Pt/V_B-C2	0.46
Pt/V_B-C3	0.79
Pt/V_N	0.61
Pt/V_N-C1	0.53
Pt/V_N-C2	0.44
Pt/V_N-C3	0.34

Table S7. LOCO cross-validation performance of PhysFormer and baseline models on the B and N catalyst series. Train R^2 and Test R^2 are bootstrap-resampled means; 95% CI denotes the bootstrap confidence interval.

Series	**Model**	**Train R^2**	**Train 95% CI**	**Test R^2**	**Test 95% CI**
B	PhysFormer	0.98	[0.95, 0.98]	0.94	[0.87, 0.97]
B	RandomForest	0.99	[0.97, 0.99]	0.90	[0.79, 0.95]
B	XGBoost	0.99	[0.98, 0.99]	0.86	[0.67, 0.96]
B	Ridge	0.02	[−0.30, 0.09]	−0.01	[−0.34, 0.09]
N	PhysFormer	0.99	[0.98, 0.99]	0.96	[0.94, 0.98]
N	RandomForest	0.99	[0.98, 0.99]	0.95	[0.90, 0.98]
N	XGBoost	0.99	[0.98, 0.99]	0.93	[0.88, 0.97]
N	Ridge	0.004	[−0.34, 0.05]	0.001	[−0.35, 0.04]

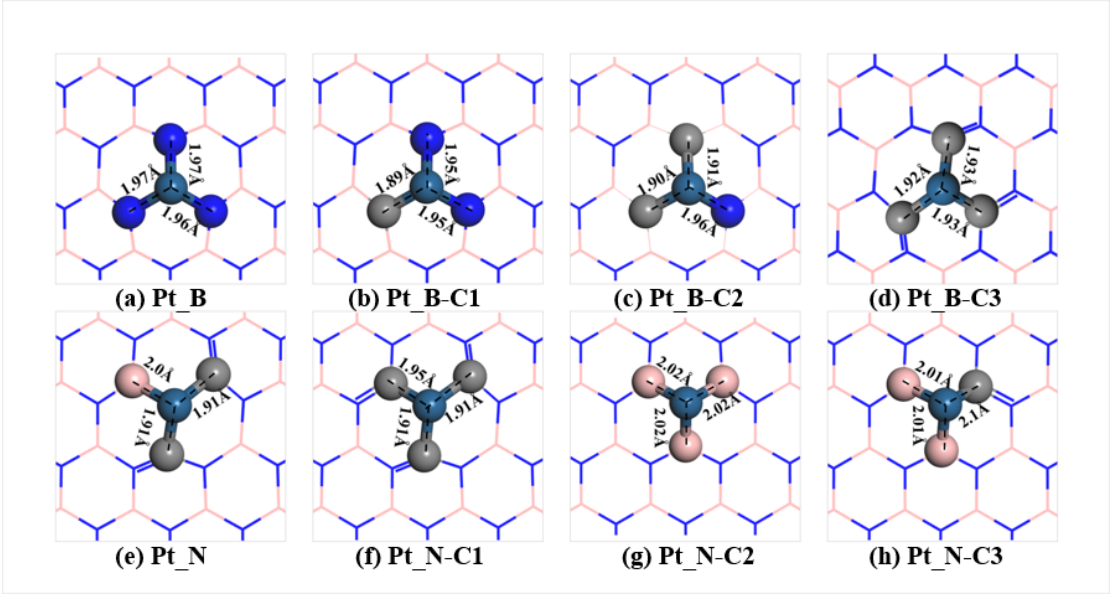

Figure S1. Optimized geometric structures of the Pt/V_B and Pt/V_N series single-atom catalyst models. Bond lengths are given in angstroms (Å). Blue, pink, gray, and light teal spheres represent nitrogen, boron, carbon, and platinum atoms, respectively.

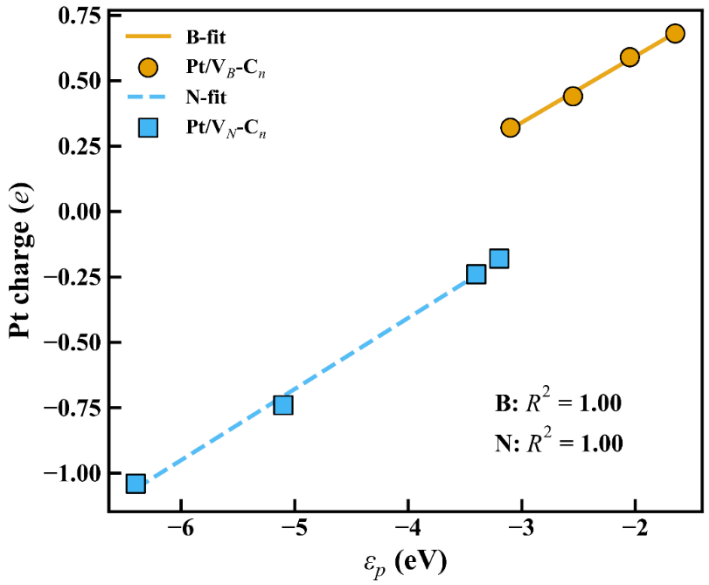

Figure S2. Correlation between the Bader charge of the Pt single atom the center-of-mass energy of the p orbital of the adjacent atom (ε_p).

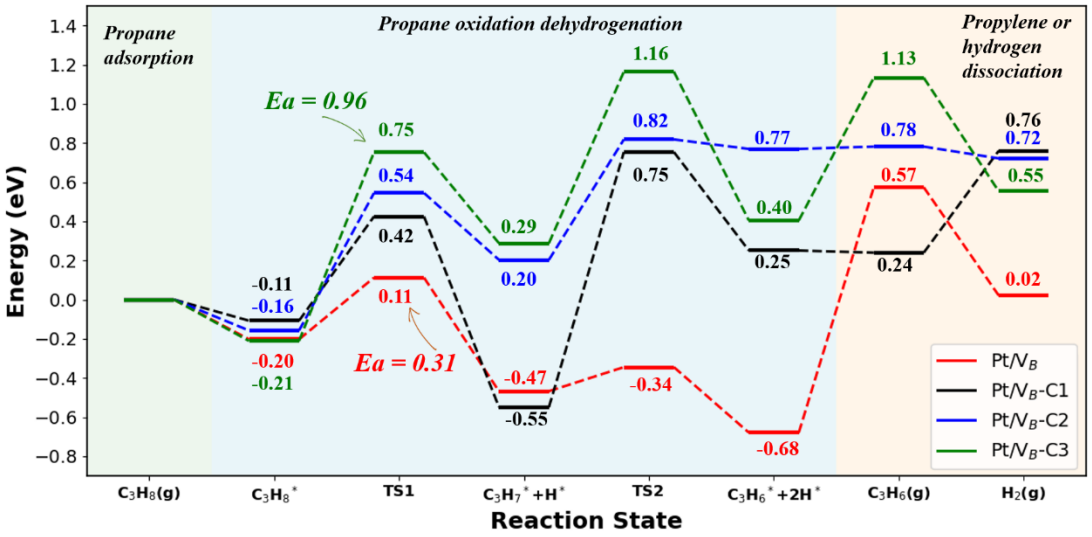

Figure S3. Calculated energy pathways for propane dehydrogenation on the Pt/V_B series catalysts. Energies are relative to the gas-phase propane molecule and the clean catalyst surface. TS1 and TS2 denote the transition states for the first and second C-H bond cleavage, respectively.

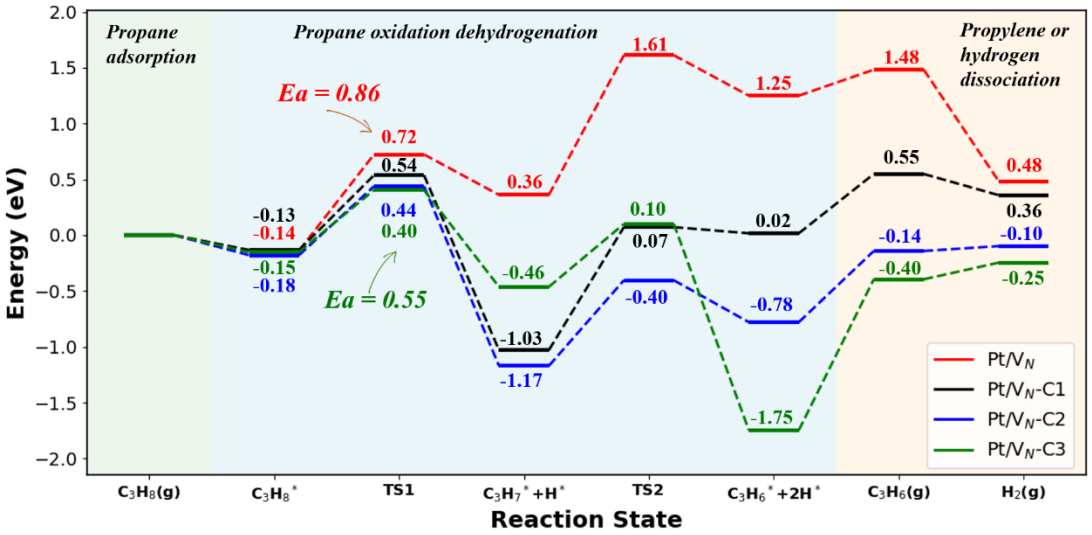

Figure S4. Calculated energy pathways for propane dehydrogenation on the Pt/V_N series catalysts. Energies are relative to the gas-phase propane molecule and the clean catalyst surface. TS1 and TS2 denote the transition states for the first and second C-H bond cleavage, respectively.

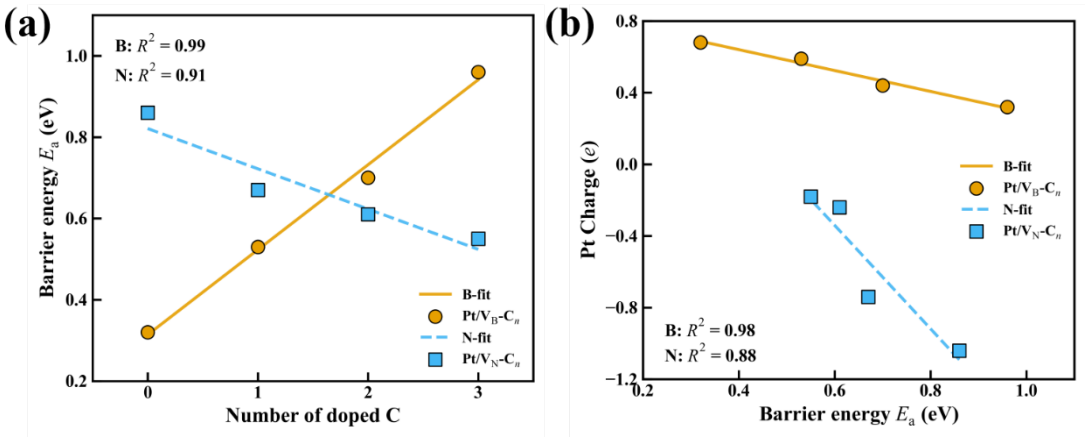

Figure S5. (a) Relationship between the barrier energy of the first C-H bond cleavage (E_a) and the number of coordinating carbon atoms (n). (b) Correlation between the barrier energy of the first C-H bond cleavage (E_a) and Bader charge of the Pt single atom

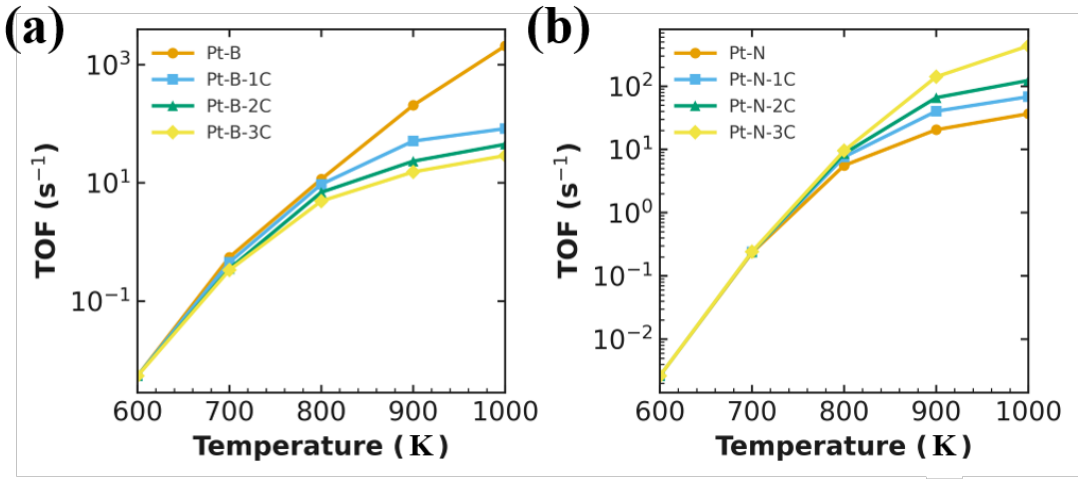

Figure S6. (a) Arrhenius plots showing the temperature dependence of the turnover frequency (TOF) for the Pt/V_B series catalysts at a constant pressure of 1 bar. (b) Arrhenius plots showing the temperature dependence of the turnover frequency (TOF) for the Pt/V_N series catalysts at a constant pressure of 1 bar.

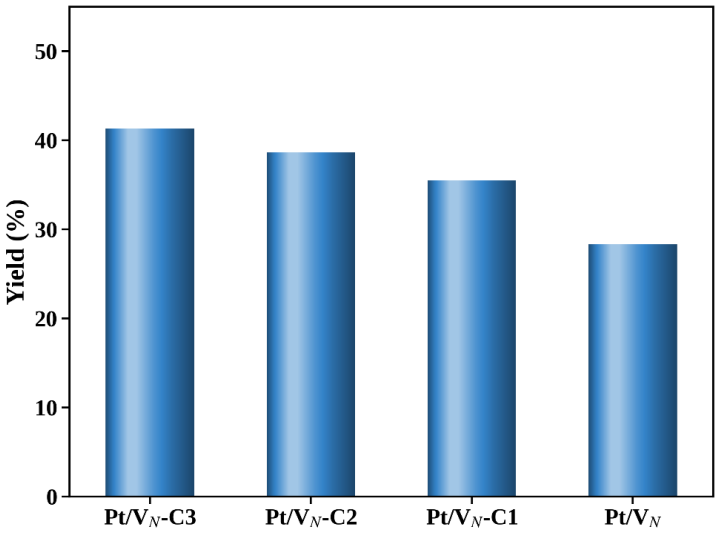

Figure S7. Plug-flow reactor predictions (Cantera, 800 K and 1 bar) comparison of Pt/V_N, Pt/V_N-C1, Pt/V_N-C2 and Pt/V_N-C3: propylene yield bar chart.

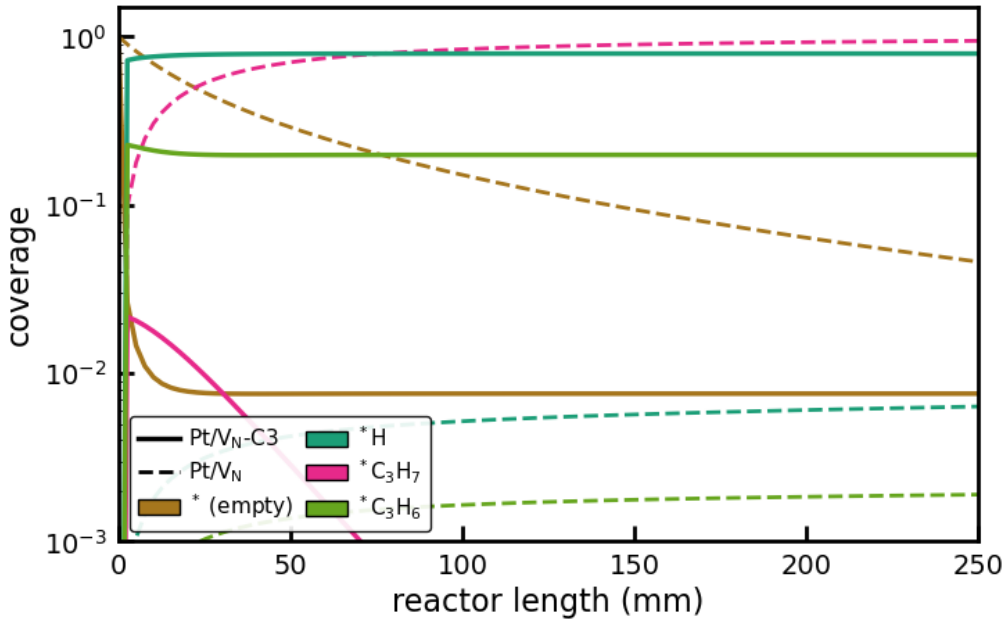

Figure S8. Cantera plug-flow simulation at 800 K and 1 bar comparing Pt/V_N: solid lines and Pt/V_N-C3: dashed lines: Corresponding surface coverages of vacant sites and key intermediates as functions of reactor length.

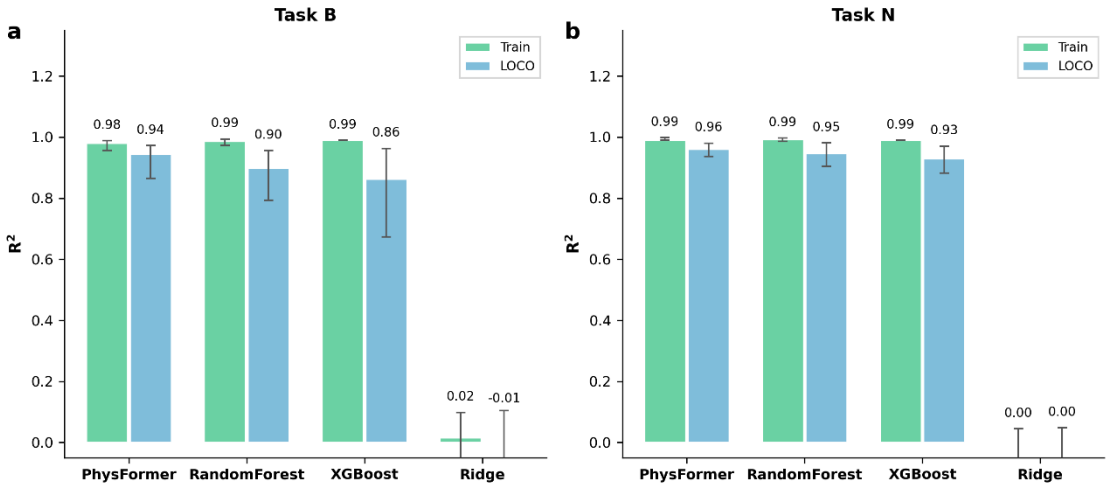

Figure S9. Model performance comparison for Pt/V_B and Pt/V_N series. Training (green) and leave-one-out cross-validation (blue) R^2 values across four models. PhysFormer achieves the best generalization performance (LOCO R^2 = 0.94–0.96) with minimal overfitting, outperforming tree-based ensembles and linear baselines.

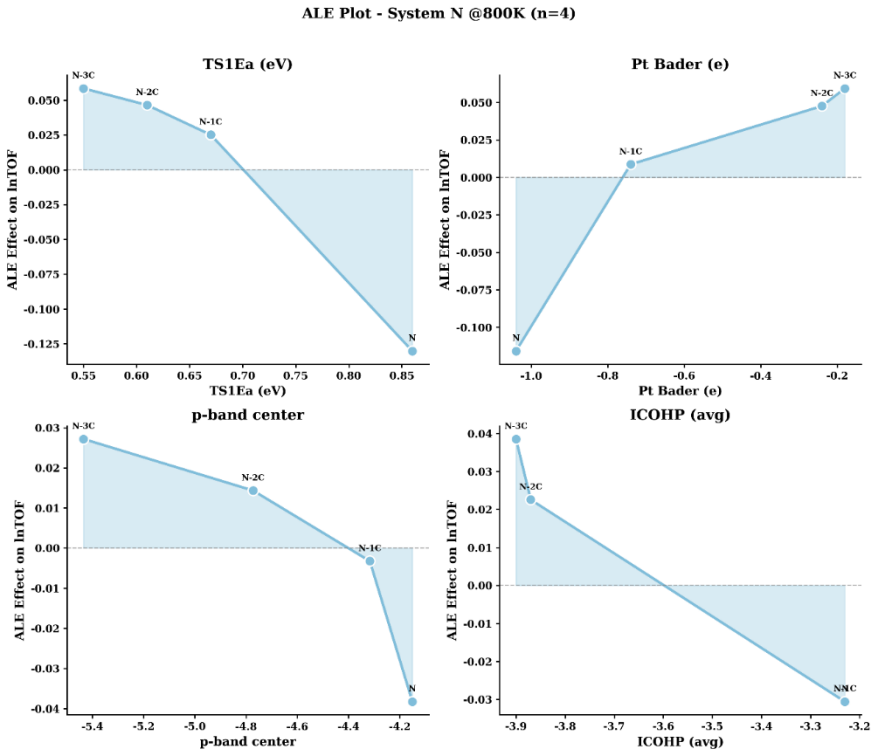

Figure S10. Accumulated local effects (ALE) analysis of the PhysFormer model for the Pt/V_B series at 800 K.

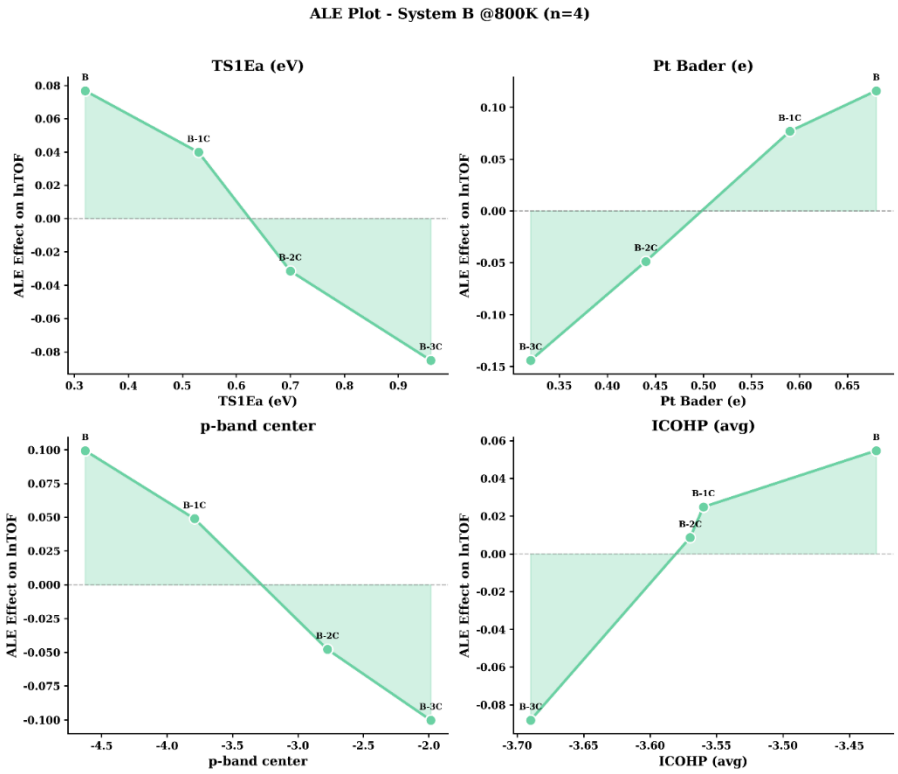

Figure S11. Accumulated local effects (ALE) analysis of the PhysFormer model for the Pt/V_N series at 800 K.

S1. PhysFormer Physical Constraint Design

To ensure physical plausibility of temperature response, this work imposes a sign constraint on the slope head $b(\mathbf{x})$:

$$b(\mathbf{x}) = -\text{softplus}(b_{\text{raw}})$$

This transformation enforces $b(\mathbf{x}) < 0$, ensuring that predicted values change monotonically with the inverse temperature variable $\tilde{u} = 1/T$, structurally avoiding non-physical phenomena such as temperature trend reversal under small-sample conditions.

Considering that real catalytic systems may deviate from ideal Arrhenius behavior (due to factors such as diffusion limitations, competitive adsorption, etc.), the model introduces a discrete temperature bias term $g(T)$ with a "cumulative increment" monotonic parameterization design: using the lowest temperature point (600 K) bias as zero baseline, biases for remaining temperature points are generated by cumulative summation of 4 non-negative increments (constrained by softplus):

$$g(T_k) = \sum_{i=1}^{k} \text{softplus}(\delta_i),\ k = 1,2,3,4;\ g(T_0) = 0$$

This design absorbs systematic temperature deviations while maintaining overall monotonic trends, and reduces non-identifiability between the baseline head $a(\mathbf{x})$ and temperature bias term. Whether to enable the temperature bias module is automatically determined through LOCO cross-validation.

S2. Hyperparameter Search Space

To ensure fair comparison, all models undergo hyperparameter optimization via LOCO-based grid search. Table S2 lists the search space and optimal configuration for each model.

S3. PhysFormer Network Architecture and Training Details

PhysFormer is built upon a multilayer perceptron (MLP), with each Trunk network layer containing Linear, LayerNorm, GELU, and Dropout modules. Input dimension is 4 (TS1Ea, Pt Bader charge, p-band center, ICOHP average), outputting to a dual-head structure. Additionally, a wide branch is introduced to establish direct linear connections from raw input, enhancing fitting capability for simple relationships.

Training employs Huber loss (β = 0.5), which is more robust to outliers compared to MSE. The optimizer is AdamW, combined with early stopping strategy (patience = 200 epochs, maximum 2000 epochs). Gradient clipping threshold is 1.0. Input descriptors are standardized and truncated to ±4 standard deviation range. The inverse temperature variable is normalized with 600 K as the reference point.

S4. Reliability Validation of PhysFormer under Small-Sample Conditions

To evaluate the generalization capability of PhysFormer under small-sample conditions, we employed a Leave-One-Catalyst-Out (LOCO) cross-validation strategy on a dataset of only 20 samples (4 catalysts × 5 temperatures). PhysFormer was systematically compared with XGBoost, RandomForest, and Ridge regression, and 95% confidence intervals were estimated via 1,000 bootstrap resamples.

In the Pt/V_B series, PhysFormer achieved a LOCO test R^2 of 0.94 (95% CI: [0.87, 0.97]), outperforming RandomForest (0.90, CI: [0.79, 0.95]) and XGBoost (0.86, CI: [0.67, 0.96]). In the Pt/V_N series, PhysFormer again ranked highest with a LOCO test R^2 of 0.96 (95% CI: [0.94, 0.98]), surpassing RandomForest (0.95, CI: [0.90, 0.98]) and XGBoost (0.93, CI: [0.88, 0.97]). Ridge regression failed to produce meaningful fits in either series ($R^2 \approx 0$).

Notably, PhysFormer not only achieved the highest LOCO R^2 in both series but also exhibited the smallest bootstrap standard deviation (0.029 for Pt/V_B series; 0.012 for Pt/V_N series), indicating high prediction stability across different catalyst partitions. In contrast, XGBoost attained a perfect training R^2 of 0.99 yet showed a substantial drop in test R^2 with a considerably wider confidence interval (Pt/V_B series CI width: 0.29 vs. 0.10 for PhysFormer), exhibiting clear signs of overfitting. The small train-test R^2 gap of PhysFormer ($\Delta = 0.04$ for Pt/V_B series; $\Delta = 0.03$ for Pt/V_N series) further confirms its strong generalization without severe overfitting under small-sample conditions.

These results demonstrate that, by incorporating physical prior knowledge, PhysFormer achieves accurate and robust predictions under the stringent setting of small-sample, leave-one-catalyst-out validation, significantly outperforming conventional machine-learning approaches.