Supplementary Information for

Pt\textsubscript{n}-O\textsubscript{v} synergistic sites on MoO\textsubscript{x}/\gamma-Mo\textsubscript{2}N heterostructure for

low-temperature reverse water–gas shift reaction

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Supplementary Methods:

Computational Methods
Spin-polarized density functional theory (DFT) calculations were carried out using the Vienna ab initio simulation package (VASP)\(^1,2\). The projector augmented-wave method\(^3\) was employed and the exchange-correlation interactions were described by the GGA-PBE functional\(^4\). The energy cutoff for plane-wave basis-set expansion was set to 500 eV. A \(1 \times 2 \times 1\) Monkhorst–Pack mesh grid\(^5\) was used to sample the Brillouin zone for structural optimization and a \(3 \times 6 \times 1\) one for calculating the density of states. The supercell contained enough vacuum layer in the vertical direction. Structural relaxations were performed until the maximum residual force on each atom was less than 0.03 eV/Å. Transition states were located by using the climbing-image nudged elastic band and the dimer methods\(^6,7\) with a force criterion of 0.10 eV/Å. Each transition state had been confirmed via vibrational mode analysis and the corresponding imaginary frequencies were listed in Supplementary Table 4. All structures were visualized using the program VESTA\(^8\).

The adsorption energy was defined by using the following expression:

\[
E_{ads} = E_{(surf+mol)} - E_{(surf)} - E_{(mol)}
\]  

(1)

where \(E_{(surf)}\) and \(E_{(mol)}\) are the energies of substrates and isolated molecules, respectively, and \(E_{(surf+mol)}\) represents the energy of the combined systems upon adsorption. It meant that a negative \(E_{ads}\) value corresponds to exothermic adsorption.

The differential charge density was calculated by using the following formula:

\[
\Delta \rho = \rho_{(surf+mol)} - \rho_{(surf)} - \rho_{(mol)}
\]  

(2)

where \(\rho_{(surf+mol)}\) is the electron density of the combined system, while \(\rho_{(surf)}\) and \(\rho_{(mol)}\) represent the electron densities of the substrate and the adsorbed molecule, respectively, with their geometries fixed as those in the combined system.

Simulation Model
In the theoretical calculations, the simulation model adopted in our previous work\(^9\)
was still employed. In brief, to construct the interface between the MoO$_3$ (010) adsorbed layers and the $\gamma$-Mo$_2$N (111) substrate, a certain degree of strain was applied to the MoO$_3$ (010) thin layers. The main change in the lattice, concretely, is to alter the angle of 32.46° in the figure below to 30.00°, to match the lattice of the $\gamma$-Mo$_2$N (111) substrate. This model well reproduced the very low formation energy of oxygen vacancies in the adsorbed MoO$_3$ (010) layers, in consistence with the experiments$^9$.

![Lattice angle of the MoO$_3$ (010) layers.](image)

In the original simulation model, a three-layer MoO$_3$ (010) and a few buffer layers of molybdenum oxide were deposited on the $\gamma$-Mo$_2$N (111) substrate, which contained seven atomic layers (Figure S15b in Supplementary Ref. 9). A Pt$_4$ cluster, which was used to represent the Pt nanoparticles in the experiments, was deposited on the MoO$_3$ adsorbed layers after the removal of one outermost oxygen atom, and in this way, a catalytic interfacial system was constructed. Compared with the simulation model in Supplementary Ref. 9, in this work, only one atomic layer, instead of the original seven atomic layers, was included in the bottom Mo$_2$N part, to decrease the computational cost in the reaction pathway exploration. Since our calculations had shown that removing a few bottom Mo$_2$N (111) layers did not change the adsorption energies of adsorbates on Pt$_4$/MoO$_3$, such a simplification of the computational model will not affect any conclusion obtained by the simulations.
Supplementary Figures:

Supplementary Figure 1. TEM pictures of all Pt-MoO$_3$/Mo$_2$N catalysts. (a, g) fresh and used pure Mo$_2$N supports; (b, h) fresh and used 0.2Pt-MoO$_3$/Mo$_2$N catalysts; (c, i) fresh and used 0.3Pt-MoO$_3$/Mo$_2$N catalysts; (d, j) fresh and used 0.5Pt-MoO$_3$/Mo$_2$N catalysts; (e, k) fresh and used 1Pt-MoO$_3$/Mo$_2$N catalysts; (f, l) fresh and used 2Pt-MoO$_3$/Mo$_2$N catalysts.
Supplementary Figure 2. HAADF-STEM images of the fresh 0.5Pt-MoO₃/Mo₂N catalyst. (a–d) 0.5Pt-MoO₃/Mo₂N before the RWGS reaction.
Supplementary Figure 3. HAADF-STEM images of the used 0.5Pt-MoO$_3$/Mo$_2$N catalyst. (a–d) 0.5Pt-MoO$_3$/Mo$_2$N after the RWGS reaction.
Supplementary Figure 4. STEM-EDS elemental mapping images of 0.5Pt-MoO$_3$/Mo$_2$N. (a) before the RWGS reaction and (b) after the RWGS reaction.
Supplementary Figure 5. The bulk phase and surface structure of 0.5Pt-MoO$_3$/Mo$_2$N. (a) XRD results of fresh and used 0.5Pt-MoO$_3$/Mo$_2$N catalysts; (b) ex situ and in situ Raman results of the 0.5Pt-MoO$_3$/Mo$_2$N catalysts.

XRD results showed that the bulk structure of the catalyst was Mo$_2$N, but the Raman results indicated that the surface structure of the catalyst was MoO$_3$, which proved the existence of a thin MoO$_3$ structure on the surface of Mo$_2$N. Meanwhile, during the RWGS reaction, the Raman signal changed from MoO$_3$ to MoO$_x$, which suggested that the surface MoO$_3$ lost oxygen and transformed to MoO$_x$ structure during the reaction.
Supplementary Figure 6. The XRD patterns of Pt-MoO$_3$/Mo$_2$N catalysts. (a) before the RWGS reaction and (b) after the RWGS reaction.
Supplementary Figure 7. Raman results of Pt-MoO$_3$/Mo$_2$N catalysts. (a) before the RWGS reaction and (b) after the RWGS reaction.
Supplementary Figure 8. The coordination structure of different samples. EXAFS spectra in $R$ space for Pt L$_3$-edge of the fresh and used Pt-MoO$_3$-Mo$_2$N catalysts. Pt foil and PtO$_2$ are used as references.
Supplementary Figure 9. Wavelet transformation (WT) EXAFS oscillation of Pt L3 edge in Pt-MoO₃/Mo₂N catalysts\(^\text{10}\). (a) fresh 0.5Pt-MoO₃/Mo₂N; (b) used 0.5Pt-MoO₃/Mo₂N after the RWGS reaction; (c) fresh 1Pt-MoO₃/Mo₂N; (d) used 1Pt-MoO₃/Mo₂N after the RWGS reaction; (e) fresh 2Pt-MoO₃/Mo₂N; (f) used 2Pt-MoO₃/Mo₂N after the RWGS reaction.

Wavelet transformation (WT) EXAFS oscillations of Pt L3 edge exhibited an increase in the intensity of Pt-Pt peak of the catalysts after the RWGS reaction compared to the catalyst before the reaction, which further indicated the aggregation of Pt atoms.
Supplementary Figure 10. EXAFS fitting results of Pt L$_3$ edge in Pt-MoO$_3$/Mo$_2$N catalysts. (a) fresh 0.5Pt-MoO$_3$/Mo$_2$N; (b) used 0.5Pt-MoO$_3$/Mo$_2$N after the RWGS reaction; (c) fresh 1Pt-MoO$_3$/Mo$_2$N; (d) used 1Pt-MoO$_3$/Mo$_2$N after the RWGS reaction; (e) fresh 2Pt-MoO$_3$/Mo$_2$N; (f) used 2Pt-MoO$_3$/Mo$_2$N after the RWGS reaction.

For all Pt-MoO$_3$/Mo$_2$N catalysts with different Pt loading, the stronger intensity of the Pt-Pt coordination peak of the used catalysts than that of the fresh catalysts was confirmed, suggesting the reduction and aggregation of the Pt species in the RWGS reaction.
Supplementary Figure 11. The chemical state of Pt species in different samples. Pt L$_3$-edge XANES spectra for the fresh Pt-MoO$_3$/Mo$_2$N catalysts. Pt foil and PtO$_2$ are used as references.
Supplementary Figure 12. Catalytic performance of various catalysts. (a) CO₂ conversion over different catalysts at various temperatures. (b) The mass specific activities of all Pt-MoOₓ/Mo₂N catalysts.

The activity of the catalyst increased with the increase of Pt loading. However, when the Pt loading exceeded 0.5%, the catalyst activity became less influenced by the Pt loading, which might be caused by the aggregation of Pt species.
**Supplementary Figure 13.** Comparison of apparent activation energy ($E_a$) over different catalysts.

The apparent activation energy ($E_a$) of catalysts with different Pt content.
Supplementary Figure 14. Experiments for the absence of mass transfer limitation over the 0.5Pt-MoO₃/Mo₂N catalyst. (a) flow rate tests. (b) particles size tests.

In this work, the particle size of the catalysts used in the catalytic tests was about 20—40 mesh. In the particle size tests, the catalysts with different particle sizes showed similar catalytic activity, indicating that the effect of mass transfer limitation in the kinetic test has been excluded (Supplementary Figure 14a). Besides, in the flow rate tests, when the gas hourly space velocity (GHSV) was above 110,000 mL⋅g⁻¹⋅h⁻¹, the effect of external diffusion could be excluded (Supplementary Figure 14b).
Supplementary Figure 15. *In situ* Raman results of 0.5Pt-MoO$_x$/Mo$_2$N. (a) under 5% H$_2$/Ar and (b) under the RWGS atmosphere.
Supplementary Figure 16. The surface structure of 0.5Pt-MoO$_x$/Mo$_2$N under the RWGS reaction.

In situ Raman results of 0.5Pt-MoO$_x$/Mo$_2$N under the RWGS atmosphere for 10 h.
Supplementary Figure 17. The surface structure of γ-Mo₂N under the RWGS reaction. *In situ* Raman tests of the pure γ-Mo₂N support under the RWGS reaction.
Supplementary Figure 18. The characterization of MoO$_3$. (a) *In situ* Raman result of MoO$_3$ under the RWGS reaction atmosphere; (b) Mo 3d XPS result of the MoO$_3$ sample.

When the MoO$_3$ sample was treated with RWGS reaction gas, the signal of MoO$_3$ did not disappear and no signal of MoO$_x$ was generated, which indicated that the surface of MoO$_3$ was difficult to be reduced during the RWGS reaction, and thus no oxygen vacancy could be generated (Supplementary Figure 18a). Meanwhile, for the MoO$_3$ sample, the Mo 3d XPS spectra only exhibited the existence of Mo$^{6+}$ (Supplementary Figure 18b), indicating that there was no oxygen vacancy on the surface of MoO$_3$. 
Supplementary Figure 19. The evolution of surface structure of 0.5Pt-MoO$_x$/Mo$_2$N under various atmospheres. *In situ* Raman tests of 0.5Pt-MoO$_x$/Mo$_2$N under various atmospheres.

As shown in Supplementary Figure 19, the Raman characteristic peaks of the MoO$_3$ disappeared when the 0.5Pt-MoO$_x$/Mo$_2$N catalyst was treated by NH$_3$, indicating the nitration for the MoO$_x$. When the nitrided surface was flowingly treated by ~3% H$_2$O/Ar, the MoO$_x$ peaks were regenerated again, reflecting the support surface was reoxidized by the low concentration of water vapor.
Supplementary Figure 20. The structural change of MoO\textsubscript{3} after the NH\textsubscript{3} treatment. (a) Color change of the MoO\textsubscript{3} sample treated with NH\textsubscript{3} flow at 300 °C for 30 min. (b) The XRD result of the MoO\textsubscript{3} sample treated with NH\textsubscript{3} flow at 300 °C for 30 min.

After the MoO\textsubscript{3} sample was treated with NH\textsubscript{3} at 300 °C for 30 min, the color of MoO\textsubscript{3} changed from white to black, indicating that the surface of MoO\textsubscript{3} was nitrated by NH\textsubscript{3} (Supplementary Figure 20a). However, the XRD results showed that the bulk phase structure of the sample was still MoO\textsubscript{3} after the treatment by NH\textsubscript{3}, which indicated that the NH\textsubscript{3} could only nitride the surface of MoO\textsubscript{3} at 300 °C rather than the bulk structure (Supplementary Figure 20b).
Supplementary Figure 21. Quasi in situ XPS spectra of 0.5Pt-MoOₓ/Mo₂N. (a, b) Mo 3d and O 1s spectra after treatment under NH₃ at 300 ºC for 10 h; (c, d) Mo 3d and O 1s spectra after treatment under NH₃ at 650 ºC for 1 h.

After the nitration of ammonia at 300 ºC, the content of oxygen atoms on the catalyst surface decreased, demonstrating the occurrence of nitration (Supplementary Figure 21b). However, after the nitration of ammonia at 650 ºC for 1 h, the presence of oxygen atoms on the surface indicated that oxygen atoms could not be completely nitrided by NH₃ treatment at 650 ºC for 1 h (Supplementary Figure 21d).
Supplementary Figure 22. Adsorption structures of a CO$_2$ molecule on different surfaces. (a, b) Pt$_4$-MoO$_x$ surface; (c) Pt$_4$-MoO$_3$ surface; (d) MoO$_x$ surface. $E_a$: adsorption energy of CO$_2$; $q$: calculated number of charges carried by CO$_2$ via the Bader charge analysis.
Supplementary Figure 23. The effect of pretreatment atmospheres on catalytic activity. The catalytic performance of 0.5Pt-MoO$_2$/Mo$_2$N after the pretreatment with 5% H$_2$/Ar and 1% O$_2$/Ar, respectively.
Supplementary Figure 24. Experiments to determine the mechanism of the RWGS reaction catalyzed by 0.5Pt-MoO$_x$/Mo$_2$N. (a) The CO$_2$ dissociation experiment of 0.5Pt-MoO$_x$/Mo$_2$N; (b) Temperature programmed surface reaction (TPSR) result of 0.5Pt-MoO$_x$/Mo$_2$N; (c, d) In situ diffused reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra of 0.5Pt-MoO$_x$/Mo$_2$N during CO$_2$ treatment and reaction conditions at 300 °C, respectively.
Supplementary Figure 25. Geometries of intermediates and transition states involved in the redox reaction pathway. The energy values in the parentheses refer to the energy barriers in the corresponding elementary steps. The Pt, Mo, C, O, and H atoms are depicted in blue, teal, gray, red, and brown, respectively.
Supplementary Figure 26. Geometries of intermediates and transition states involved in the formate reaction pathway. The energy values in the parentheses refer to the energy barriers in the corresponding elementary steps. The Pt, Mo, C, O, and H atoms are depicted in blue, teal, gray, red, and brown, respectively.
Supplementary Tables:

**Supplementary Table 1.** Physical properties of the 0.5Pt-MoO$_3$/Mo$_2$N catalyst.

| Catalyst             | Loading (wt.%) | BET surface area (m$^2$/g) |
|----------------------|---------------|----------------------------|
| 0.5Pt-MoO$_3$/Mo$_2$N| 0.59$^a$      | 78.1                       |

$^a$Determined by ICP-AES.
### Supplementary Table 2. Structure parameters obtained from the EXAFS fitting.

| Sample               | Shell  | Bond length (Å) | Coordination Number | $\sigma^2$ (Å$^2$) | $E_0$ shift (eV) | R-factor ($\times 10^{-3}$) |
|----------------------|--------|-----------------|---------------------|-------------------|-----------------|-----------------------------|
|                      | Pt-O   | 2.04            | 3.5                 | 0.008             | 6.7             | 17.7                        |
| 0.5Pt-MoO$_3$/Mo$_2$N-fresh | Pt-O   | 2.03            | 2.1                 | 0.005             |                 |                             |
|                      |        |                 |                     |                   | 8.7             |                             |
|                      | Pt-Pt  | 2.84            | 1.6                 | 0.007             |                 |                             |
|                      |        |                 |                     |                   | 17.8            |                             |
| 1Pt-MoO$_3$/Mo$_2$N-fresh | Pt-O   | 2.04            | 2.9                 | 0.004             |                 |                             |
|                      |        |                 |                     |                   | 11.8            | 15.7                        |
|                      | Pt-Pt  | 2.83            | 2.1                 | 0.005             |                 |                             |
|                      |        |                 |                     |                   |                 |                             |
| 1Pt-MoO$_3$/Mo$_2$N-used | Pt-O   | 2.03            | 1.8                 | 0.012             |                 |                             |
|                      |        |                 |                     |                   | -5.8            | 18.2                        |
|                      | Pt-Pt  | 2.84            | 2.6                 | 0.006             |                 |                             |
|                      |        |                 |                     |                   |                 |                             |
| 2Pt-MoO$_3$/Mo$_2$N-fresh | Pt-O   | 2.02            | 2.2                 | 0.008             |                 |                             |
|                      |        |                 |                     |                   | 6.9             | 17.9                        |
|                      | Pt-Pt  | 2.85            | 2.5                 | 0.009             |                 |                             |
|                      |        |                 |                     |                   |                 |                             |
| 2Pt-MoO$_3$/Mo$_2$N-used | Pt-O   | 2.03            | 1.2                 | 0.002             |                 |                             |
|                      |        |                 |                     |                   | 9.3             | 21.9                        |
|                      | Pt-Pt  | 2.84            | 3.0                 | 0.007             |                 |                             |
**Supplementary Table 3.** Comparison of RWGS reaction for the as-prepared and literature reported catalysts.

| Catalyst                        | H₂:CO₂ | Temperature (°C) | Pressure (MPa) | Rate (10⁻⁵ molCO/gcat/s) |
|---------------------------------|--------|------------------|----------------|--------------------------|
| 0.5Pt-MoOₓ/Mo₂N                 | 3:1    | 250              | 0.1            | 7.7                      |
| 0.5Pt-MoOₓ/Mo₂N                 | 3:1    | 300              | 0.1            | 17.2                     |
| Cu/β-Mo₂C                       | 2:1    | 300              | 0.1            | 7.3                      |
| Cu–Zn–Al                        | 2:1    | 300              | 0.1            | 1.5                      |
| Pt/CeO₂                         | 3:1    | 300              | 0.1            | 1.2                      |
| AuMo/SiO₂                       | 2:1    | 300              | 0.8            | 0.6                      |
| In₂O₃–CeO₂                      | 2:1    | 300              | 0.1            | 0.1                      |
| NiAu/SiO₂                       | 3:1    | 340              | 0.1            | 0.8                      |
| Pt–CeO₂                         | 4:1    | 400              | 0.1            | 4.8                      |
| TiO₂/Cu                         | 3:1    | 400              | 0.1            | 1.8                      |
| SiO₂/Cu                         | 3:1    | 400              | 0.1            | 1.1                      |
| Pt–TiO₂                         | 1:1    | 400              | 0.1            | 0.5                      |
| Rh@S-1                          | 3:1    | 450              | 1.0            | 0.3                      |
| Ni–in–Cu                        | 3:1    | 500              | 0.1            | 4.0                      |
| NiAu/SiO₂                       | 3:1    | 500              | 0.1            | 2.7                      |
| K₈₀–Pt/L                        | 1:1    | 500              | 0.1            | 2.2                      |
| K₂₀₀–Pt/L                       | 1:1    | 500              | 0.1            | 0.9                      |
| In₂O₃–CeO₂                      | 2:1    | 500              | 0.1            | 0.3                      |
**Supplementary Table 4.** Imaginary frequencies of all the transition state in the energy profiles shown in Figure 4f.

|                  | TS  | TS1 | TS2 | TS3 | TS4 | TS5 | TS6 |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| **Redox IF (cm⁻¹)** | 318.8 | 29.6 | --  | --  | --  | --  | 1045.4 |
| **Carboxyl IF (cm⁻¹)** | 953.6 | 260.6 | 867.7 | --  | --  | --  | --    |
| **Formate IF (cm⁻¹)** | 413.8 | 236.1 | 660.0 | 190.8 | 521.2 | 1045.4 |
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