

Supplementary

Unlocking the Potential of Zr_4N_4 Catalyst for CO_2 Dissociation Mechanism into CO and HCOOH

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1. Conversion test for computational parameters.

1.1. Cut-off energy conversion test

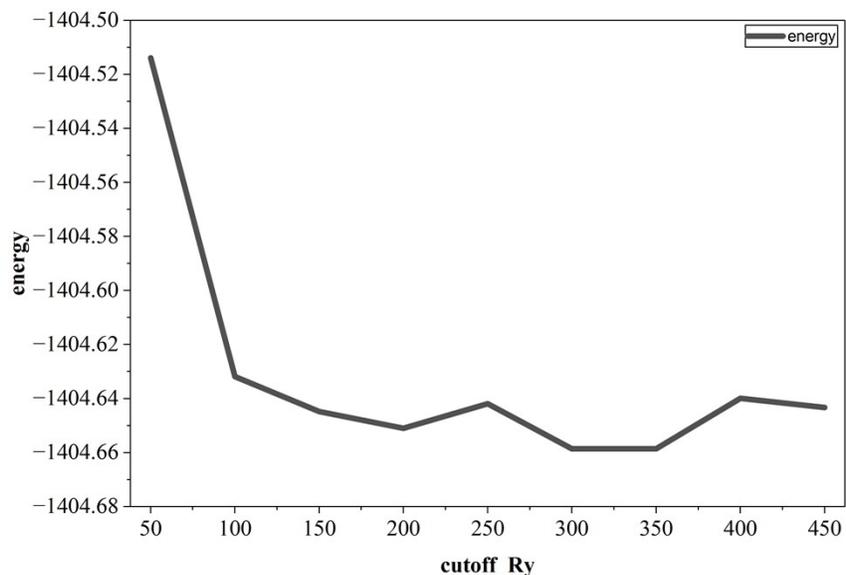


Figure S1: Cut-off energy conversion test diagram.

In order to confirm the accuracy of the results obtained from the calculations, a convergence test for the cut-off energy of the mesh was performed. The energy of the system was calculated for different values of the cut-off energy ranging from 50 Ry to 450 Ry, as shown in Figure S1. It is confirmed from the results obtained from the calculations that the energy of the system diminishes rapidly for lower values of the cut-off energy. As the cut-off energy increases, the energy of the system becomes stable.

The total energy changes from 50 Ry to 250 Ry is approximately **-1404.51 Ry** to **-1404.64 Ry**. This represents a percentage variation of approximately **0.0093%**.

In this higher range, the energy fluctuates between **-1404.64 Ry** and **-1404.65 Ry**. This corresponds to a much smaller percentage variation of approximately **0.0007%**.

The overall variation in total energy across the entire tested range is extremely small, on the order of **10^{-2} Ry**.

While the energy shows reasonable convergence at **200 Ry**, we have selected a kinetic energy cutoff of **450 Ry** for the final calculations. This higher value is employed to strictly eliminate the "**egg-box effect**" spurious oscillations in the energy and forces caused by the movement of atoms relative to the underlying finite grid-ensuring maximum numerical precision for the reaction pathways.

Therefore, a cut-off energy of 450 Ry is chosen for the calculations.

1.1. Vacuum conversion test

In order to avoid the possibility of interaction between the periodic images in the non-periodic direction, a convergence calculation in the thickness of the vacuum layer was carried out. For this purpose, the thickness of the vacuum layer was varied between 5 Å and 13 Å, and the total energy of the system in each case was computed, as shown in Figure S2.

As shown in the figure, the total energy changes appreciably when the thickness of the vacuum layer increases from 5 Å to 7 Å. This suggests that the interaction between the periodic images is quite appreciable in the case where the thickness of the vacuum layer is 5 Å. However, as the thickness of the vacuum layer increases further, the change in the total energy becomes negligible.

The total energy changes from 5 Å to 7 Å is approximately **-1411.58 Ry** to **-1405.5 Ry**. This represents a percentage variation of approximately **0.43%** and from 7 Å to 9 Å is approximately **-1405.5 Ry** to **-1404.67 Ry**. This represents a percentage variation of approximately **0.05%**.

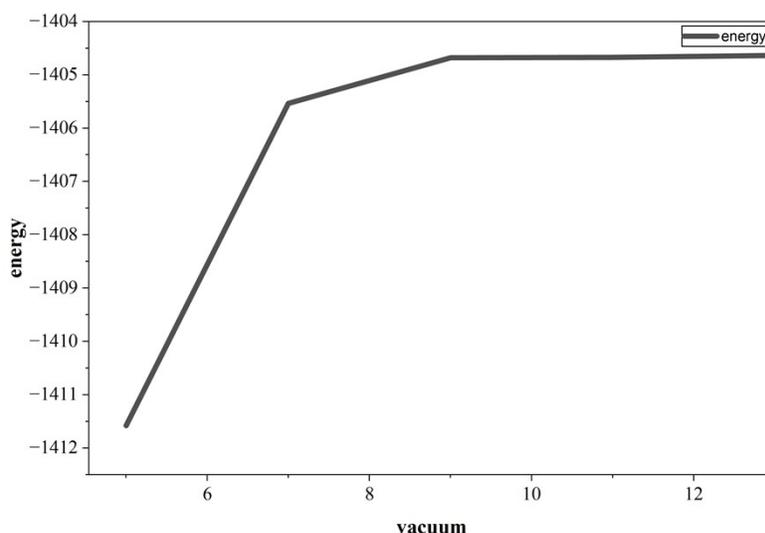


Figure S2: Vacuum conversion test diagram.

So, the total energy remains nearly constant when the thickness of the vacuum layer exceeds 9 Å. Therefore, a 9 Å thickness of the vacuum layer is used in the entire calculation in order to obtain the results accurately and efficiently.

1.3. Basis Set conversion test

In order to decide upon an appropriate basis set for calculations, convergence tests were performed for different basis sets, including single ζ (SZ), double ζ (DZ), single ζ polarized (SZP), and double ζ polarized (DZP) basis sets. For this purpose, the total energy of the optimized structure calculated by each basis set was compared.

The calculated total energy for each basis set is as follows:

For SZ, it is -1399.0776 eV

For DZ, it is -1401.6590 eV

For SZP, it is -1403.8126 eV

For DZP, it is -1404.6433 eV

As can be seen, an increase in basis set size results in a significant decrease in the total energy.

The largest decrease in energy is found when increasing from SZ to DZ, and then from DZ to SZP; however, when increasing from SZP to DZP, the change is relatively smaller, suggesting that it is close to convergence. Therefore, DZP was chosen for all calculations.