

Electronic Supplementary information: Effect of Al-distribution on oxygen activation over Cu-CHA

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The 52 configurations

As the Al-sites can be assumed to be evenly distributed in the framework, all feasible configurations with two Al^{3+} in the hexagonal unit cell have been considered. Taking into account the structural symmetry and Löwenstein’s rule (Al-O-Al links are forbidden), we obtain 52 different configurations, which are listed in Table S1. The Site labels refer to the numbering in Figure 1 in the main text.

Table S1: Description of the 52 configurations where two Si^{4+} are replaced by Al^{3+} . The site labels refer to the numbering in Figure 1 in the main text.

Conf.	Site labels						
1	11 + 13	14	11 + 14	27	11 + 15	40	11 + 26
2	0 + 6	15	12 + 19	28	11 + 7	41	0 + 25
3	0 + 2	16	11 + 10	29	11 + 29	42	11 + 22
4	11 + 20	17	0 + 23	30	0 + 15	43	11 + 21
5	0 + 12	18	11 + 19	31	0 + 17	44	0 + 26
6	12 + 14	19	12 + 15	32	11 + 16	45	0 + 31
7	0 + 10	20	0 + 7	33	0 + 24	46	0 + 28
8	0 + 3	21	0 + 18	34	0 + 22	47	0 + 32
9	0 + 13	22	0 + 8	35	12 + 22	48	0 + 34
10	0 + 20	23	11 + 24	36	0 + 29	49	0 + 27
11	0 + 19	24	0 + 14	37	0 + 21	50	11 + 28
12	0 + 9	25	0 + 16	38	11 + 17	51	0 + 33
13	11 + 23	26	12 + 16	39	12 + 21	52	11 + 27

Thermodynamic integration of free-energy gradients

Constrained molecular dynamics is performed at 273 K to obtain the free-energy barriers for oxygen activation over $\text{Cu}(\text{NH}_3)_2^+$ -pairs. This simulation is performed for 10 ps with a time step of 0.5 fs. Thermodynamic integration of free-energy gradients has been used to calculate the free energy difference between two states in the activation of O_2 . Suppose the reaction path can be described via a set of vectorial geometric coordinates $\xi = \{\xi_k; k = 1, \dots, r\}$. The free-energy difference between these two states can be calculated by

$$\Delta A_{1 \rightarrow 2} = \int_{\xi(1)}^{\xi(2)} \left(\frac{\partial A}{\partial \xi} \right)_{\xi^*} \cdot d\xi \quad (1)$$

The free-energy gradients $\left(\frac{\partial A}{\partial \xi} \right)_{\xi^*}$ were determined from constrained *ab-initio* MD simulations using the equation^{S1-S5}

$$\left(\frac{\partial A}{\partial \xi_k} \right)_{\xi^*} = \frac{1}{\langle |\mathbf{Z}|^{-1/2} \rangle_{\xi^*}} \langle |\mathbf{Z}|^{-1/2} [-\lambda_{\xi_k} + k_B T G] \rangle_{\xi^*} \quad (2)$$

where k_B is the Boltzmann constant and T is the simulation temperature. Here, the Lagrange multiplier λ is employed to determine the $\left(\frac{\partial A}{\partial \xi} \right)_{\xi^*}$ for the full range of ξ with sufficient statistical precision via SHAKE algorithm.^{S6} \mathbf{Z} is defined by

$$\mathbf{Z} = \sum_i \frac{1}{m_i} \left(\frac{\partial \xi}{\partial \mathbf{r}_i} \right)^2 \quad (3)$$

and it is a mass metric tensor, which can compensate the bias introduced by the constraint using the blue-moon ensemble approach.^{S7} G is a factor to eliminate the explicit dependence on the generalized coordinates complementary to ξ .^{S8}

A CHA hexagonal unit cell which includes 36 Si atoms in tetrahedral (T) positions is used to perform constrained MD to investigate the free energy barrier of O₂ activation on the pairs. In this structure, two Si (label 11 and 28 in table S1) are replaced by two Al, which leads to a Si to Al ratio of 17. It is shown that the two barriers (Figure S1) are similar with the corresponding ones simulated in the small CHA unit cell with lower Si/Al ratio (Figure 2 in the manuscript). Therefore, the Si to Al ratio seems have minor effects on the O₂ activation over the Cu⁺ pairs.

We also simulate the O₂ dissociation from the activated state over the pairs in CHA by constrained AIMD. The geometric constraint for this case is the O-O distance from 1.48 Å to 2.33 Å. The free energy difference for this step is shown in Figure S2. The barrier is similar with the previously reported^{S9} 0.28 eV barrier from climbing NEB for this step.

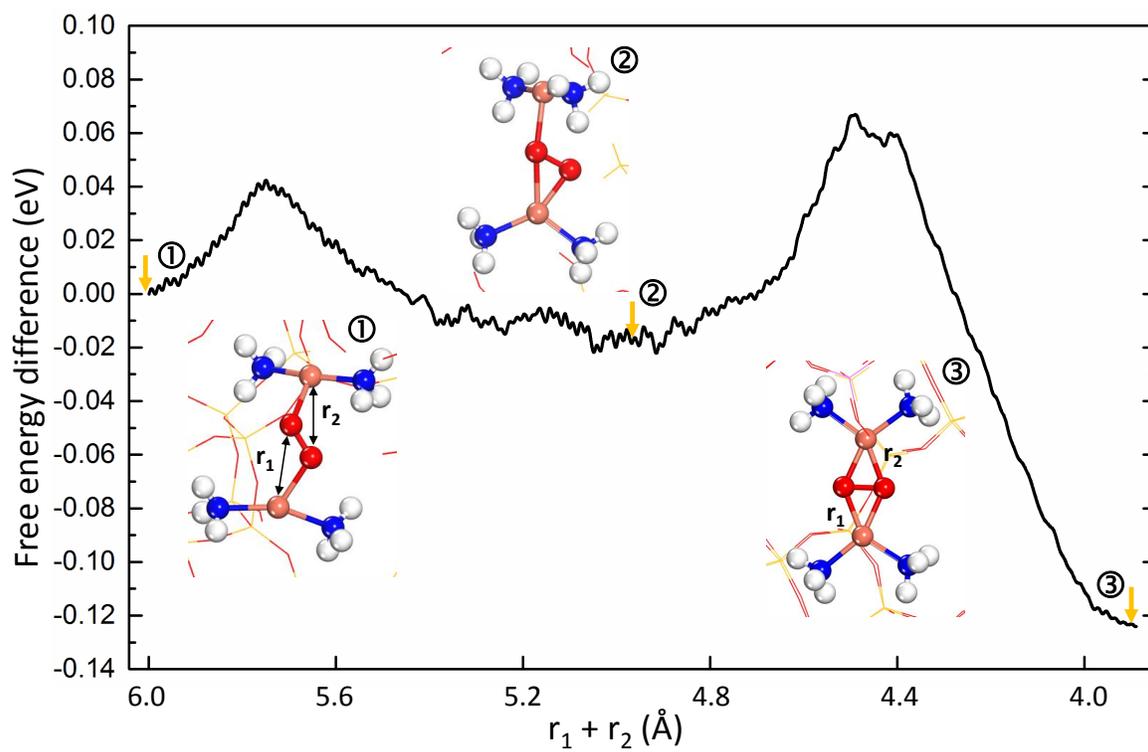


Figure S1: Free energy difference for oxygen activation over the Cu^+ -pairs in a hexagonal Cu-CHA unit cell from constrained molecular dynamics simulation. The structures in the insets marked with numbers correspond to times along the trajectory. Atom color codes are same as in Figure 2 of the main text.

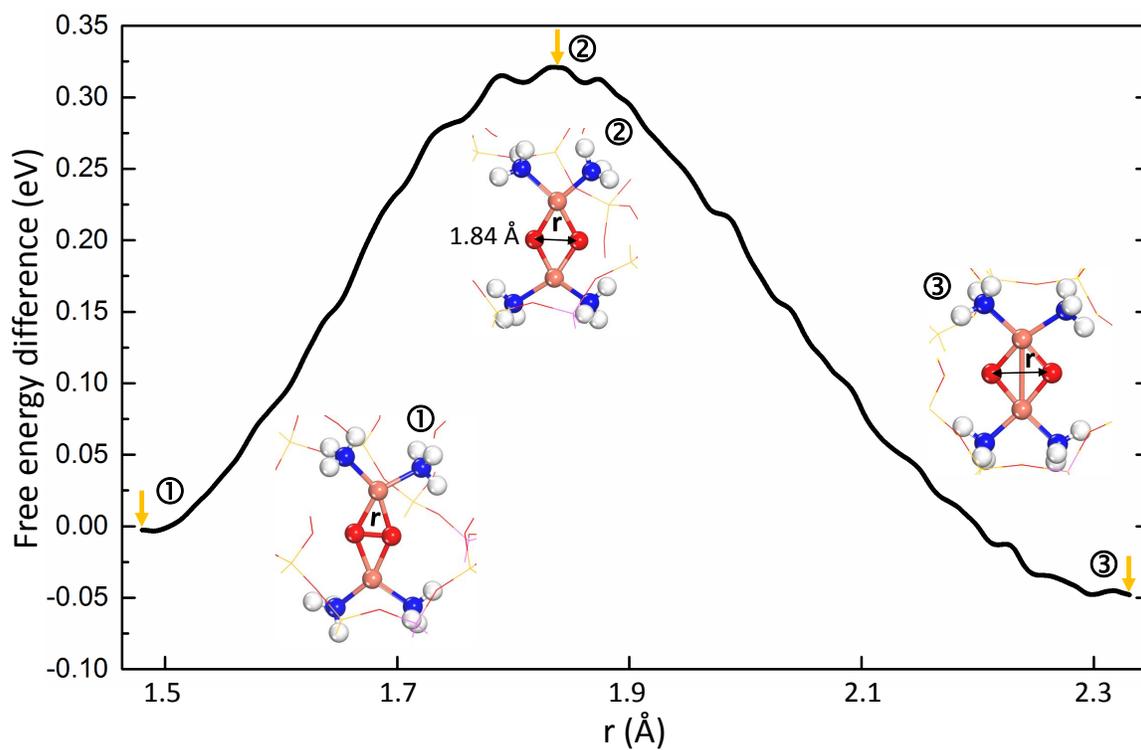


Figure S2: Free energy difference for the oxygen dissociation over the Cu^+ -pairs in a rhombohedral CHA unit cell from constrained molecular dynamics simulations. The structures in the insets marked with numbers are corresponding to the numbers with yellow arrows at the curves. Atom color codes are same with Figure 2 in the main text.

Triplet-Singlet spin-crossing

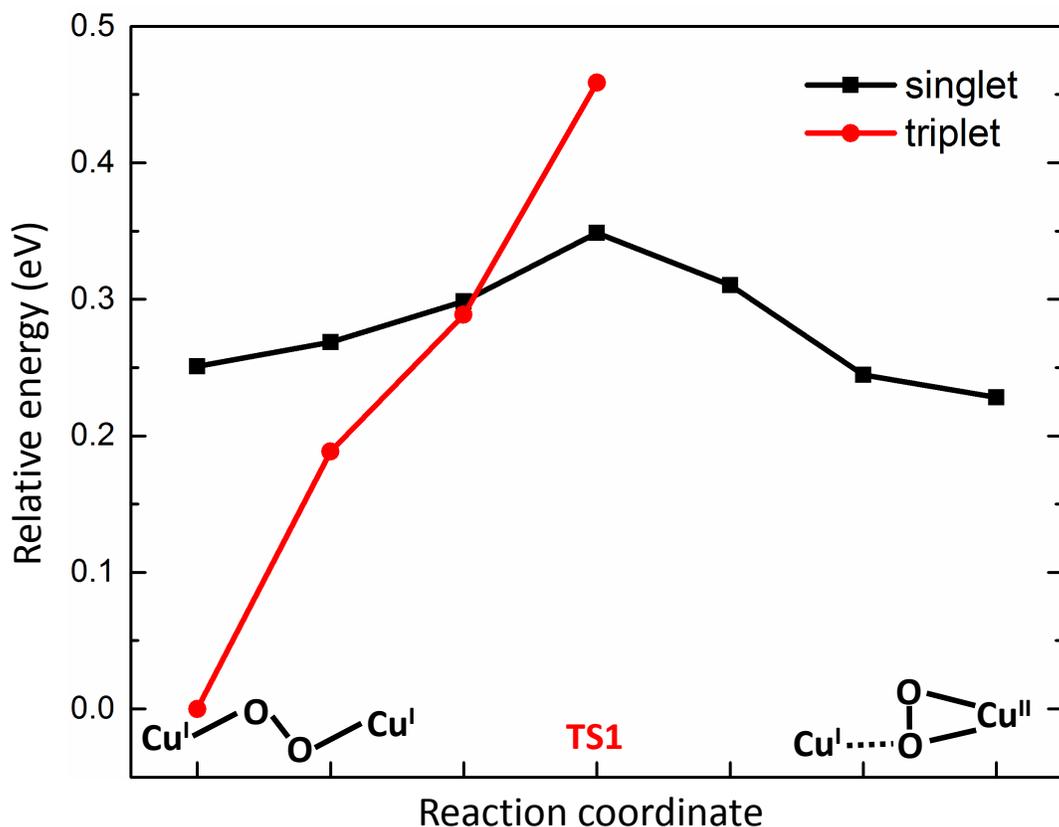


Figure S3: Triplet and singlet potential energy curves for dissociation of O₂ during the first step where O₂ is rotated and CuO₂Cu takes a planar structure. The singlet curve is obtained by climbing image NEB calculations and reported with the Cu-O-O-Cu as reaction coordinate. TS1 stands for the transition state.

The activation of O₂ involves a spin flip from triplet to singlet. In order to map out the potential energy surfaces in detail, we show the singlet and triplet curves in Figure S3. The triplet curve is, except for the initial configuration, based on the singlet structures. The two curves cross just before the transition state (TS1).

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