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Supporting Information

Theoretical investigation into the effect of water on the N_2O decomposition reaction over Cu-ZSM-5 catalyst

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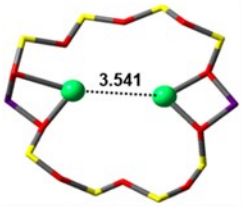
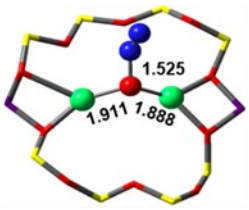


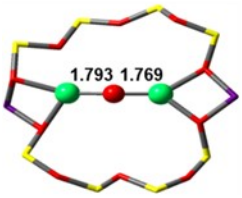
$A_{(s)}$

$B_{(s)}$



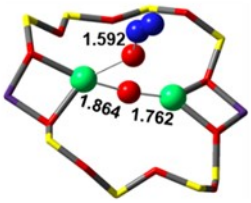
$TS_{BC(s)}$

$C_{(t)}$

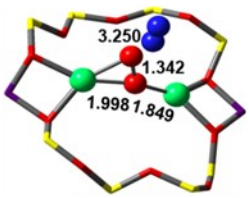


$D_{(t)}$

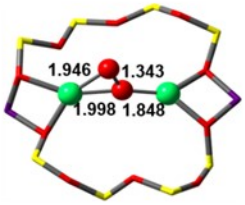
$E_{(t)}$



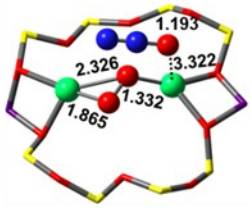
$TS_{EF(t)}$



$F_{(t)}$

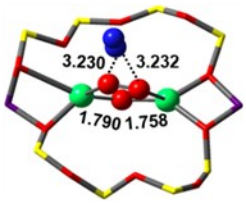


$G_{(t)}$

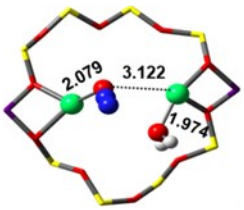


$H_{(t)}$

$TS_{HI(t)}$

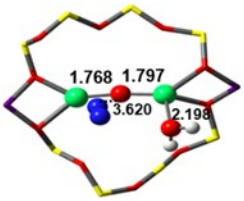


$I_{(t)}$

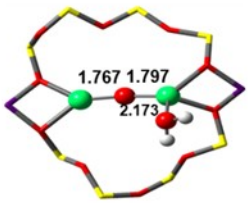


$B_{w(s)}$

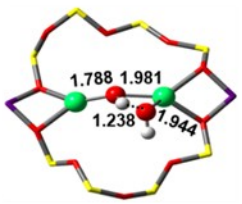
$TS_{BCw(s)}$



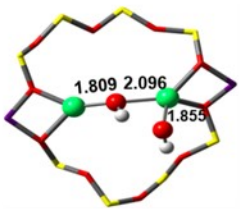
$C_{w(t)}$



$D_{w(t)}$



$TS_{1W(t)}$



$1_{W(t)}$

$2_{W(t)}$

$TS_{23W(t)}$

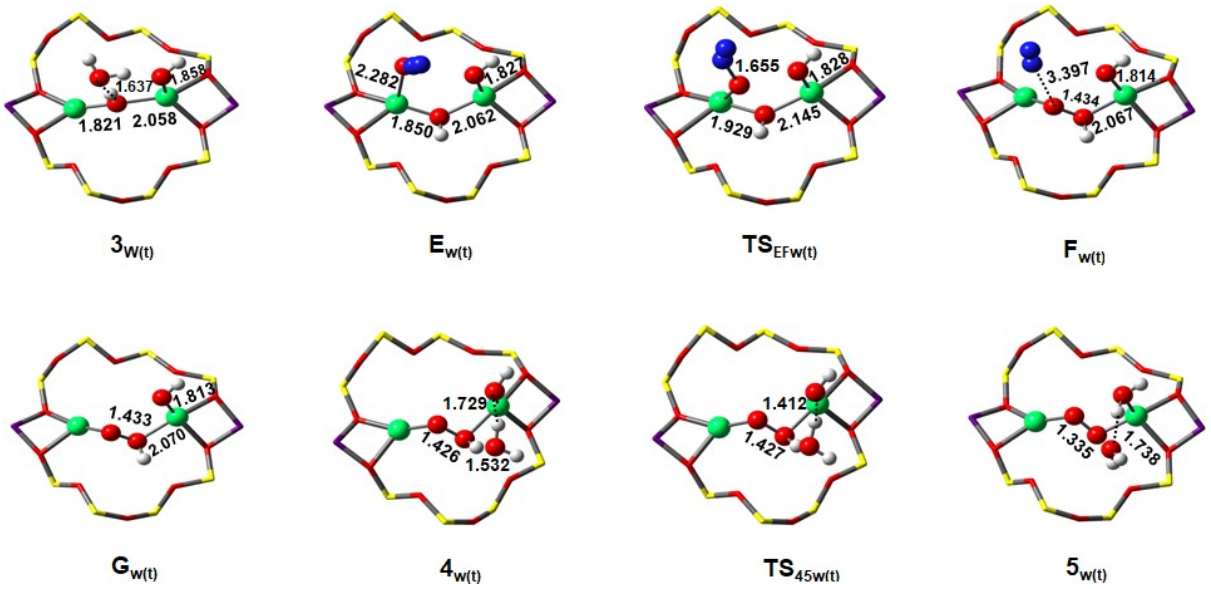


Fig. S1 10-membered QM layer from the optimized geometries of intermediates and transition states involved in the N_2O decomposition. Selected bond distances are in Å.

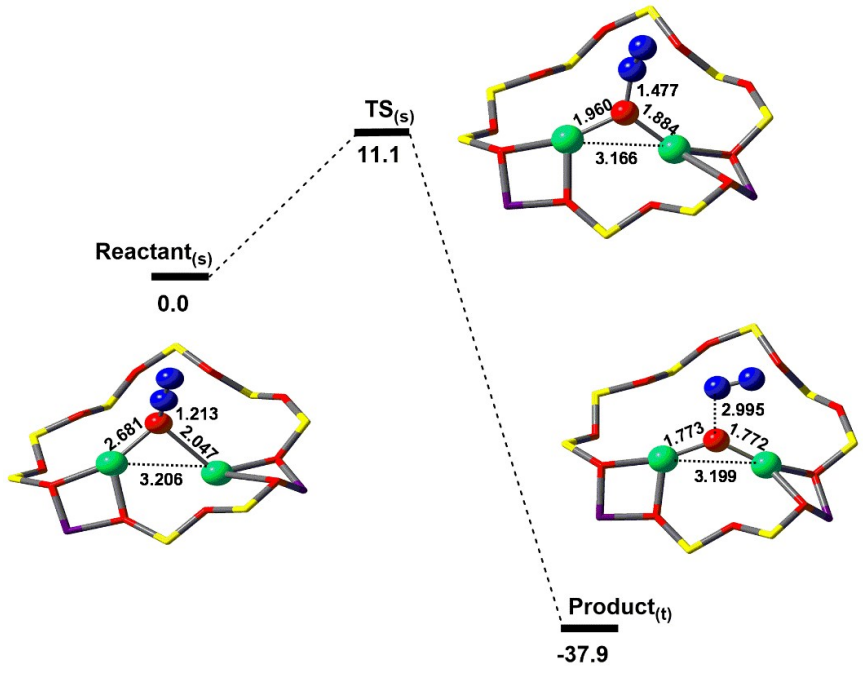
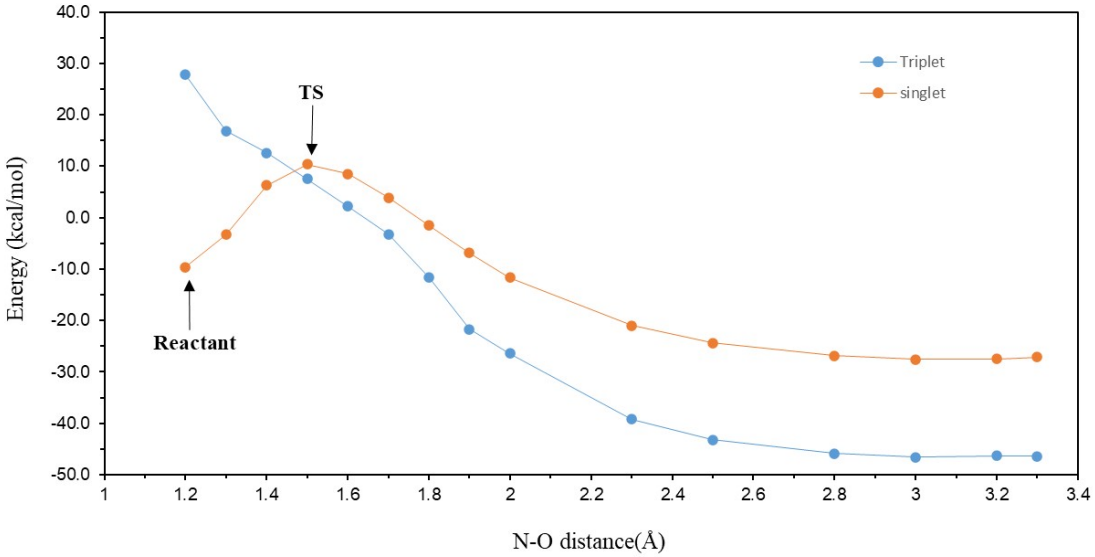
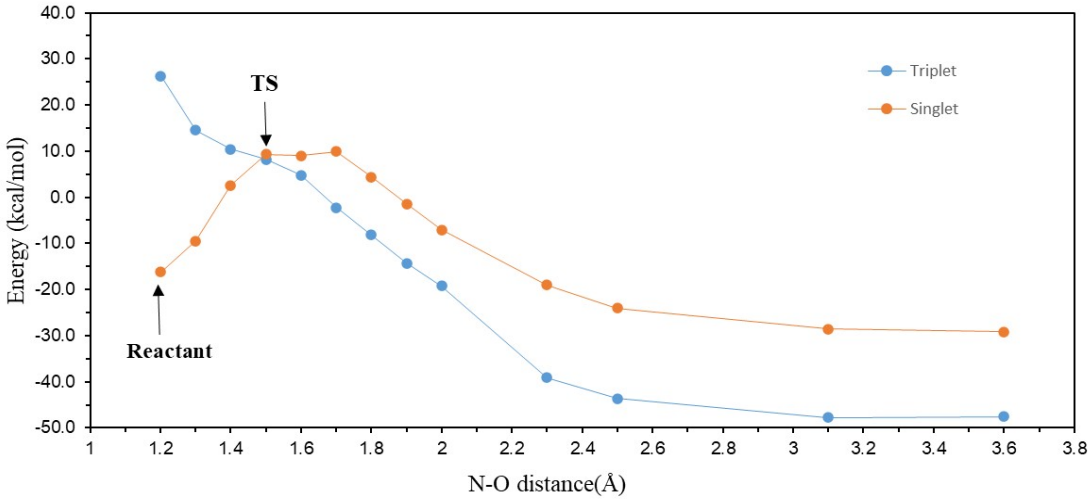


Fig. S2 Structural changes and corresponding reaction energy barriers for N_2O decomposition on **2T** model. The relative energies are in kcal/mol. The selected bond distances are in Å. The spin state of the corresponding structure is given in parentheses, where s and t represent closed-shell singlet and triplet state, respectively.

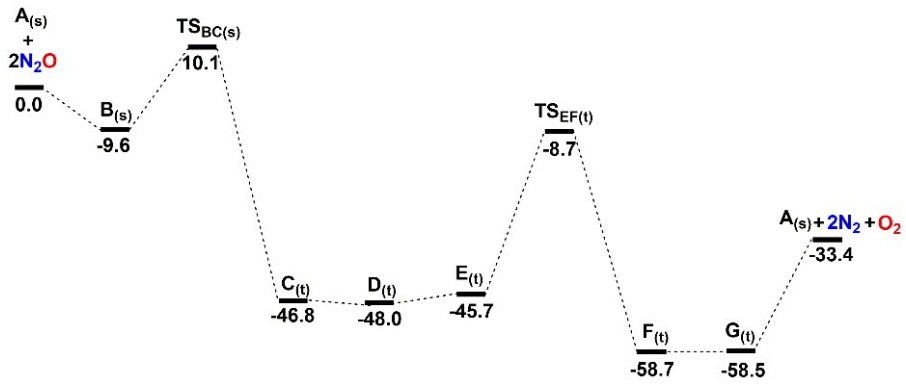


(a)

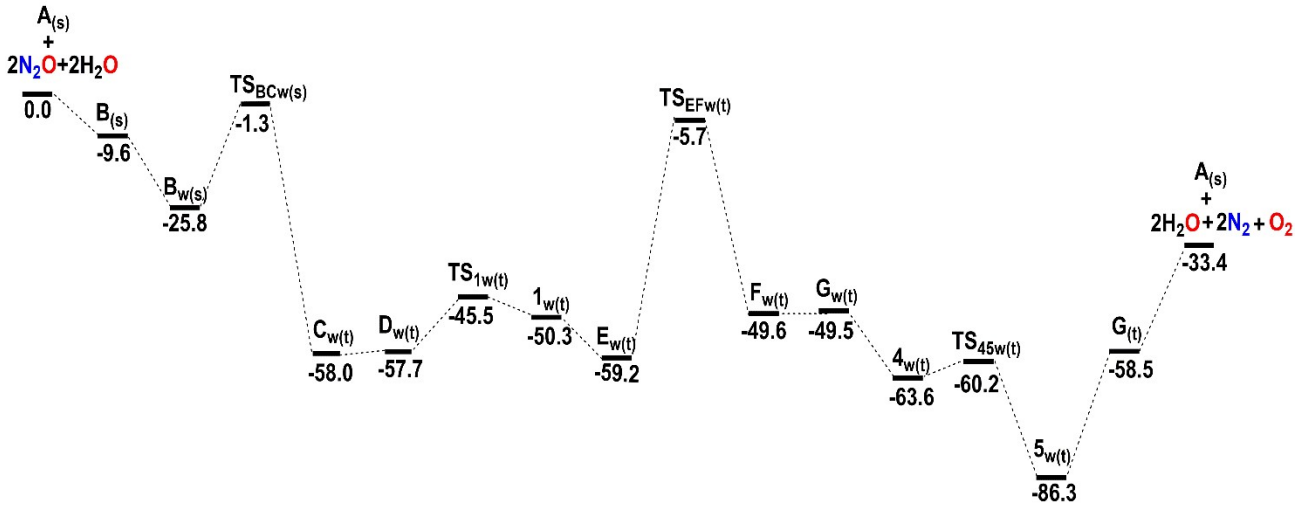


(b)

Fig. S3 Calculated singlet and triplet potential energy surface of decomposition of N_2O over bare dicopper active site **(a)** In the absence of water **(b)** In the presence of coadsorbed water.



(a)



(b)

Fig. S4 The overall energy profile diagram of (**a**) N_2O decomposition in the absence of water (**b**) N_2O decomposition in the presence of coadsorbed water. The relative energies are in kcal/mol.

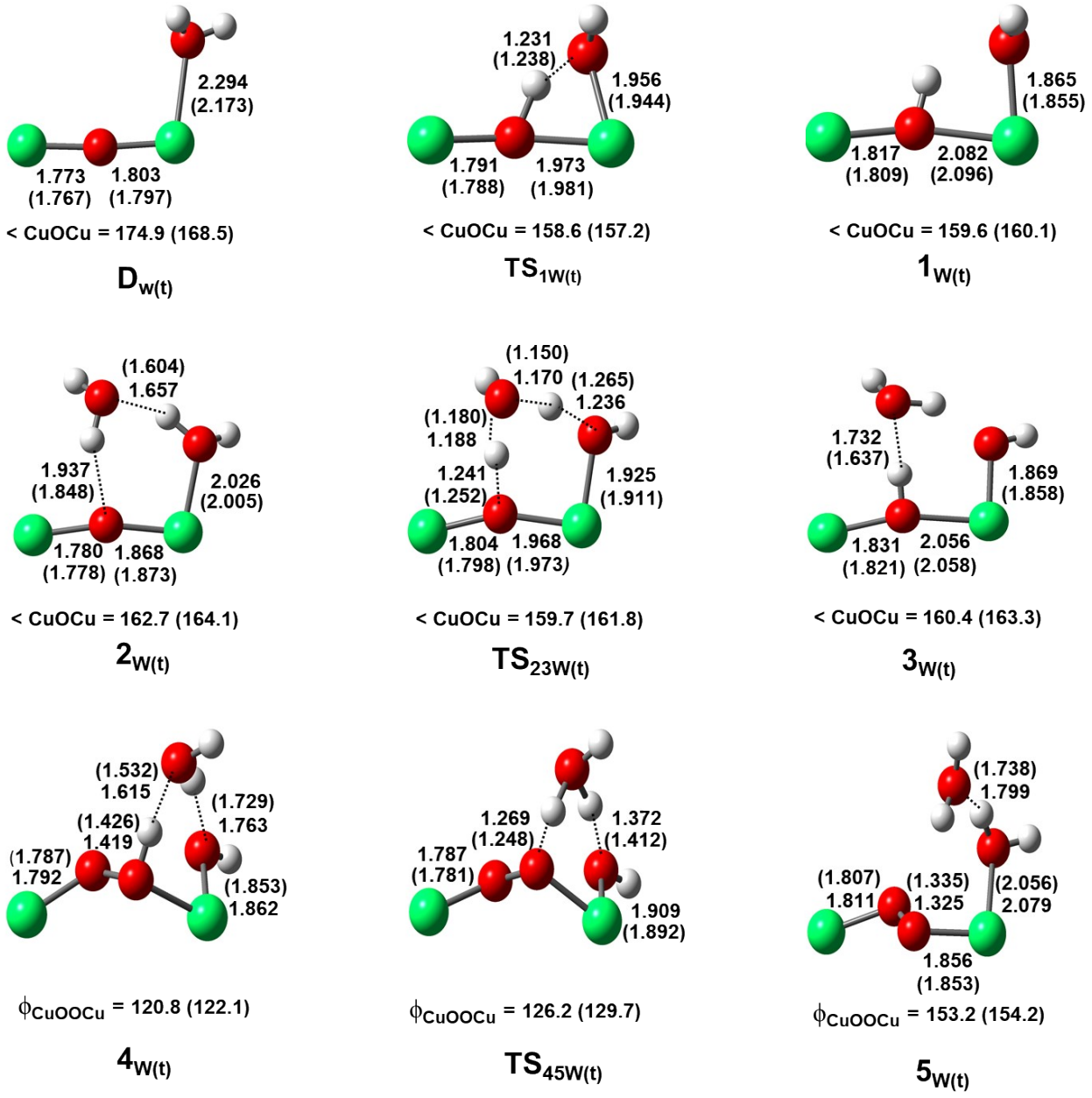


Fig. S5 Selected geometrical parameters of the representative structures of intermediates and transition states calculated at the ONIOM (B3LYP/6-311++G(d,p):UFF) level of theory. The selected bond distances (Å) and angles (degree) are indicated. The values in parentheses show the corresponding values obtained at the ONIOM (B3LYP/GEN:UFF) level of theory.

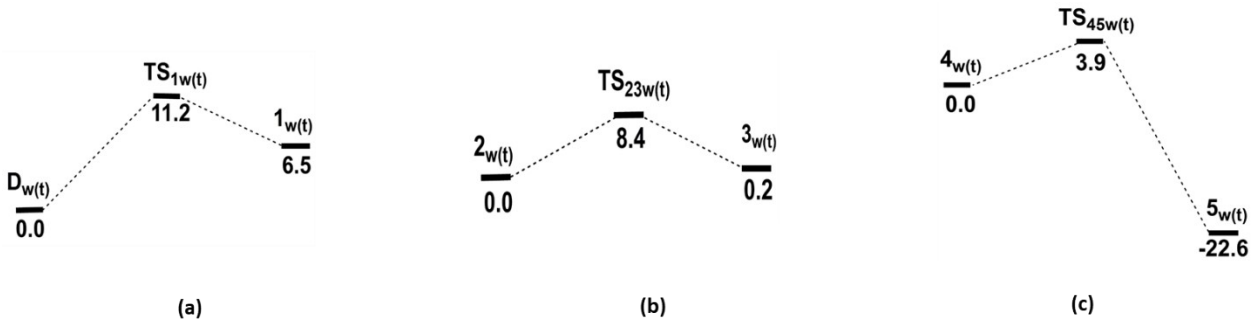


Fig. S6 Energy profile diagrams for **(a)** Formation of $[Cu–(OH)–Cu(OH)]^{2+}$ centers **(b)** H_2O assisted proton transfer, and **(c)** Regeneration of $[Cu….Cu]^{2+}$ calculated at the ONIOM (B3LYP/6-311++G(d,p):UFF) level of theory. All values are in kcal/mol.